STUDY OF NANOSTRUCTURES AND INTERFACES
OF TECHNOLOGICAL MATERIALS
BY MEANS OF ELECTRON MICROSCOPY TECHNIQUES

PhD thesis

by

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Submitted to “Department of Physics, Aristotle University of Thessaloniki”

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THESSALONIKI 2016
Dedicated to

my family & Stavros
Περίληψη

Το MOS τρανζίστορ ή MOSFET, είναι ένα τρανζίστορ επίδρασης πεδίου, ευρέως διαδεδομένο για χρήση ως ενισχυτής ή διακόπτης ηλεκτρονικών σημάτων. Μία άλλη κατηγορία τρανζίστορ επίδρασης πεδίου, το τρανζίστορ υψηλής ευκινησίας ηλεκτρονίων (High Electron Mobility Transistor (HEMT)), είναι ιδανικό για εφαρμογές σε υψηλές συχνότητες με χαμηλό συντελεστή θορύβου. Πιο συγκεκριμένα, ενσωματώνει μία ετεροεπαφή μεταξύ δύο υλικών διαφορετικών ενεργειακών χασμάτων, με αποτέλεσμα τη δημιουργία ενός διδιάστατου αερίου ηλεκτρονίων (2DEG) υψηλής ευκινησίας/ταχύτητας κοντά στη διεπιφάνεια. Τα τελευταία χρόνια, τρανζίστορ HEMT βασιζόμενο σε Gallium Nitride (GaN) προσελκύουν το ενδιαφέρον της επιστημονικής κοινότητας, αφού τα χαρακτηριστικά του GaN το καθιστούν ιδανικό για εφαρμογές υψηλούς ισχύος και συχνότητας. Μέχρι σήμερα, η επιταξιακή ανάπτυξη του GaN πραγματοποιείται κυρίως χρησιμοποιώντας ξένα υποστρώματα, όπως το πυρίτιο (Si), το καρβίδιο του πυριτίου (SiC) και ο σάπφειρος (Al2O3), εξαιτίας του αυξημένου κόστους των εγγενών υποστρωμάτων. Πιο συγκεκριμένα, το SiC παρουσιάζει πολύ καλές ιδιότητες όσον αφορά τη θερμική αγωγιμότητα και τις μικρές αποκλίσεις στη σταθερά πλέγματος με το GaN. Από την άλλη, το πυρίτιο (Si (111)), παρόλο που παρουσιάζει μεγαλύτερες αποκλίσεις στην σταθερά πλέγματος με το GaN, συνδυάζει τα πλεονεκτήματα του χαμηλού κόστους και της θερμικής σταθερότητας. Επιπλέον, σε κάθε τύπο υποστρώματος, είναι απαραίτητη η ανάπτυξη των στρώματων με μία απόκλιση κατά μία μικρή γωνία από το επίπεδο (0001), για οικονομικούς κυρίως σκοπούς.

Στη διατριβή αυτή, μελετήθηκαν με τεχνικές ηλεκτρονικής μικροσκοπίας δομές που αποτελείτο από ομοεπιταξιακά ανεπτυγμένα στρώματα 4H-SiC σε υποστρώματα 4H-SiC off για εφαρμογές MOS διατάξεων (MOSFET), όπου αναζητήθηκαν τα χαρακτηριστικά και η ποιότητα του υμενίου. Χρησιμοποιώντας τη μέθοδο χημικής μηχανικής επιπεδοποίησης (CMP), επιτεύχθηκε μία λεία-καλής ποιότητας διεπιφάνεια SiO2/4H-SiC, χωρίς να παρουσιάζει ατέλειες (προκαλούμενες από την επιταξιακή ανάπτυξη). Επιπλέον, η δομή αυτή παρουσίαζε μία αυξημένη τιμή τάσης κατάρρευσης του οξείδιο. Προκειμένου να μειωθεί η αυξημένη πυκνότητα διεπιφανειακών καταστάσεων μεταξύ του οξείδιο SiO2 και του στρώματος 4H-SiC, η οποία προκαλεί τη μείωση της απόδοσης του καναλιού, μετά την εναπόθεση πραγματοποιήθηκε ανόπτηση σε περιβάλλον N2O ή POCl3. Το οξείδιο, μετά την ανόπτηση σε περιβάλλον POCl3, παρουσίασε εμφανώς καλύτερη επιπεδοποίηση της επιφάνειας, σε σχέση με αυτή σε περιβάλλον N2O, πιθανώτατα εξαιτίας της σημαντικής και ομοιογενούς διάχυσης φωσφόρου στο οξείδιο αυτό.

Επιπλέον, μελετήθηκαν πολύστρωματικές δομές AlGaN/GaN επιταξιακά ανεπτυγμένες σε υποστρώματα Si (111) και (0001) SiC (4H-6H) (on axis και off axis), με τη μέθοδο MOCVD. Όσον αφορά την ετεροεπιταξία σε Si (111), τα τρία διαβαθμισμένα στρώματα AlGaN (76%, 35%, 19% Al) που εισήχθησαν μεταξύ των GaN στρώματον, λειτούργησαν ως φίλτρα ατελειών, αποτρέποντας τη διάδοση των νηματοειδών εξαρμοσέων (threading dislocations-TD) προς την AlGaN/GaN ετεροεπαφή και έτσι την υποβάθμιση της ποιότητας του καναλιού.
2DEG. Η επιφάνεια της buffer δομής, σε κάθε περίπτωση (on axis, off axis), ήταν λεία, χωρίς ρωγμές, ιδανική για την ανάπτυξη της AlGaN/GaN ετεροεπαφής και την υλοποίησή του τρανζίστορ HEMT. Επικινδυνεύοντας παρόλη την ύπαρξη των βαθμίδων, τελικά, η επιφάνεια της ετεροεπαφής παρουσίασε V-σχηματισμούς, εξαιτίας αφηρέμισης (strain relaxation).

Όσον αφορά την ετεροεπιταξία σε υποστρώματα SiC, στα on-axis δείγματα, παρατηρήθηκε μία μεγαλύτερη πυκνότητα νηματοειδών εξαρμόσεων, σε σχέση με τα off-axis. Σε κάθε περίπτωση, παρατηρήθηκε οτι ένας σημαντικός αριθμός των ατελειών αυτών σχηματίζει βρόγχους εξαρμόσεων και εξαλείφεται, χωρίς να προσεγγίζει την ετερεπαφή. Επιπλέον, το στρώμα AIN, ανεπτυγμένο πάνω στο υπόστρωμα, εμφάνισε V-σχηματισμούς με πλευρικά τοιχώματα τα επίπεδα (1011). Οι σχηματισμοί αυτοί, κατά την εναπόθεση του επόμενου στρώματος GaN, υπερκαλύπτονται από αυτό, εξαιτίας των διαφορών στην διαδοχή των στρώσεων, παρατηρήθηκε τη δημιουργία ατελειών με την ονομασία «stacking mismatch boundaries» στα σημεία των βαθμίδων, επάγοντας τον σχηματισμό των V-ατελειών. Επιπλέον, χρησιμοποιώντας προηγμένες τεχνικές μικροσκοπίας, η ύπαρξη ενός μονοατομικού στρώματος Ga αποκαλύφθηκε στη διεπιφάνεια AIN/SiC. Συγκρινόντας τα on και off-axis δείγματα, η επιφάνεια της AlGaN/GaN ετεροεπαφής παρουσίασε την καλύτερη μορφολογία (επίπεδη) στην περίπτωση των off-axis, παρόλη την ύπαρξή των βαθμίδων. Τελικά, προτάθηκαν μοντέλα για την περιοχή των βαθμίδων (περιστώσεις με ασήμαντη αλλά και έντονη παραμόρφωση) στη διεπιφάνεια AIN/SiC, βασιζόμενα στον δομικό χαρακτηρισμό και στα αποτελέσματα της ποσοτικής ανάλυσης που πραγματοποιήθηκε. Τα αποτελέσματα της προσομοίωσης παρουσίασαν καλή ταύτιση με τα πειραματικά αποτελέσματα, επιβεβαιώνοντας την εγκυρότητα των προτεινόμενων μοντέλων.
Abstract

The MOS transistor or MOSFET is a field effect transistor (FET), used for amplifying or switching electronic signals. A type of FET, the High Electron Mobility Transistor (HEMT), incorporating a heterojunction between two different bandgap materials where the 2DEG formation takes place, provides high levels of performance as compared to previous technologies. The last years, Gallium Nitride HEMTs have attracted much attention, being ideal for high-power and high-frequency electronics. So far, GaN epitaxy is carried out using foreign substrates, due to the expensive native substrates. More specifically, Silicon Carbide (SiC) is a very good choice for GaN heteroepitaxy, in terms of thermal conductivity and small lattice mismatch to GaN. However, Si (111) substrates offer the advantages of lower cost and thermal stability, although presenting a decreased lattice mismatch to GaN. Moreover, in GaN epitaxy, due to materials economy reasons, a lower off cut substrate is essential.

Similarly, in SiC homoepitaxy (used for metal-oxide-semiconductor capacitors (MOS) based device applications), studies were carried out in order to manage the growth of a good crystal quality epilayer on a 2 deg cut off 4H-SiC material. After CMP process, a good quality smooth SiO$_2$/4H-SiC interface without epitaxial-induced defects was obtained, presenting an increased value of the oxide electric breakdown field. In order to reduce the large interface-states concentration at the SiO$_2$/SiC interface, post-deposition-annealing processes in N$_2$O or POCl$_3$ were used. The oxide layer treated in POCl$_3$ exhibited a higher degree of planarization in respect to the N$_2$O treatment situation, probably as a consequence of the strong incorporation of Phosphorus in it during annealing procedure. Thus, the results of this study obviously pave the way to the 2 deg off oriented SiC substrates device fabrication.

Furthermore, the structural characterization of AlGaN/GaN multilayer structures heteroepitaxially grown on Si (111) and SiC (4H, 6H) substrates (on axis and off axis) by MOCVD method, was carried out using electron microscopy techniques.

Concerning heteroepitaxy on Si (111) substrates, the step graded AlGaN buffer layers inserted in between the GaN layers, behaving as a defect filter, prevented the threading dislocations (TDs) reaching the AlGaN/GaN heterostructure and negatively affecting the 2DEG channel electron density. Finally, a crack-free smooth surface of the final GaN epitaxial layer was achieved in on and off axis cases, making the buffer structure ideal for the forthcoming growth of the heterostructure. The growth of the AlGaN/GaN heterostructure on top presented V-shaped defects, due to strain relaxation reasons. The AlN interlayer grown in between the heterostructure presented V-shaped defects, due to strain relaxation reasons. The AlN interlayer grown in between the heterostructure presented an almost uniform thickness and clear interfaces.

Concerning heteroepitaxy on “on” and "off-axis” SiC substrates, a higher density of TD was observed in the on axis, as compared to the misoriented one, although not reaching the heterostructure in both cases. V-shaped defects (trenches) are formed into the AlN nucleation layer (with (101) sidewalls), completely overgrown by GaN. Due to the stacking sequence mismatch, stacking mismatch boundary defects were observed in the steps positions of SiC/AlN interface, inducing the V-defect (trench formation). The off-cut of 2 deg gives the best morphology (atomically flat) of the AlGaN barrier and GaN cap layers, despite the steps
existing. By using advanced microscopy techniques, a monolayer of GaN was revealed in the SiC/AlN nucleation layer interface. Finally, a model of the stepped-strained SiC/AlN interface was build, based on the structural characterization and quantitative analysis results. The simulation results of the structure coincided well with the experimental HRTEM results, proving the accuracy of the proposed model and analysis.
Introduction

The motivation of this thesis derived from the fact that so far SiC homoepitaxy is carried out on 8-deg-off or 4-deg-off SiC substrates and GaN heteroepitaxy on almost on-axis (up to 0.3 deg off) SiC substrates. However, as 6-inch SiC wafers are already introduced in the market, a decrease of the substrate off-cut to 2 deg for SiC homoepitaxy is desirable to reduce the manufacturing costs. Thus, if both, GaN heteroepitaxy and SiC homoepitaxy are successfully introduced onto 2-deg-off SiC substrates, this would pave the way to monolithic integration of both kinds of devices on a common platform of SiC. Moreover, high cost and limited diameter-scalability of SiC and other substrates fuel also the research for the GaN-on-silicon (111) approach.

Thus, in this PhD thesis, the study of AlGaN/GaN multilayer nanostructures heteroepitaxially grown on “on axis” and off axis silicon (Si) and silicon carbide (4H-SiC and 6H-SiC) substrates is presented, using conventional, high resolution and other advanced electron microscopy techniques. These structures are used in High Electron Mobility Transistor (HEMT) device applications. More specifically, studying the structural characteristics of each one of the layers of the multilayer structure as well as the interfaces in between them is very important as they critically affect the 2-dimensional electron gas (2DEG) properties formed in the AlGaN/GaN heterostructure, and thus determine the overall HEMT device quality characteristics.

Moreover, the structural properties of SiC epilayers homoepitaxially grown on 2 deg 4H-SiC substrates are studied, used for metal oxide semiconductor (MOS) based applications. More specifically, the crystal quality of 2 deg cut off material, surface roughness, surface defects and the effect of CMP on the layers properties are throughout discussed and finally associated with the electrical characteristics of the structures.

The multilayer structures on Si (111) and SiC were grown in the Institute of High Pressure Physics “Unipress” and TopGaN Ltd, in Warsaw, Poland, and the SiC epilayers on SiC substrates in NOVAsiC & CNR, under LastPower European Union program. The structural characterization (TEM-HRTEM) of the samples was performed at the Electron Microscopy Laboratory of Department of Physics, in Aristotle University of Thessaloniki, in Greece. The advanced microscopy techniques characterization was performed at Electron Microscopy for Materials Science (EMAT), at University of Antwerp in Belgium, under ESTEEM2 European Union program.

The first three chapters contain the theoretical part of this thesis. More specifically, in the 1st chapter of this thesis, the group III-V nitride properties are presented, as well as the important phenomenon of polarization that they exhibit, determining the 2DEG formation in the AlGaN/GaN heterostructure. Moreover, the importance of the substrate polarity is discussed and the way it affects the epilayers growth. Finally, techniques for epitaxial growth of III-V nitrides on foreign SiC substrates and the most used substrates for nitride epitaxy are presented. In the 2nd chapter of this thesis, the structure, operation principle and applications of HEMT devices is presented. The 2DEG formation mechanism and some 2DEG formation...
suppression factors are discussed. In the 3rd chapter of this thesis, the operation principle of STEM microscopy is discussed.

The chapters 4-7 contain the experimental part of this thesis. More specifically, in the 4th chapter of this thesis, the experimental results concerning the structural characteristics of MOS capacitors grown on 2 deg 4H-SiC substrates, using N₂O or POCl₃ post-deposition annealing processes are presented. Moreover, the effect of chemical mechanical planarization process (CMP) on the structural and electrical characteristics of the structure is discussed. In the 5th chapter of this thesis, the experimental results concerning the AlGaN/GaN heterostructures grown on “on axis” and off axis Si substrates are presented. More specifically, the structural characteristics (using TEM and HRTEM techniques) of each one of the layers of the multilayer structure and of the interfaces in between and their possible effect in the 2DEGs channel properties are discussed. The effect of the substrate offcut on the overall structure properties is studied. In the 6th chapter of this thesis, the experimental results concerning the AlGaN/GaN heterostructures grown on “on axis” and off axis SiC substrates are presented. More specifically, the structural characteristics (using TEM, HRTEM and STEM-HAADF combined with EDX techniques) of each one of the layers of the multilayer structure and of the interfaces in between and their possible effect in the 2DEGs channel properties are discussed. Moreover, the chemical characterization of layers and interfaces using STEM-EDX method gives us the appropriate information for the chemical composition of elements of the structure. The effect of the substrate offcut on the overall structure properties is studied in this case too. Finally, some important AFM results and electrical characteristics results are presented. In the 7th chapter of this thesis, a quantitative analysis of the stepped interface between SiC substrate and the first grown layer (AlN) is presented. Furthermore, the building of models is discussed, based on the structural characterization and quantitative analysis results. Finally, the simulation results of the structure are obtained and compared to the experimental HRTEM results.

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Chapter 1: Group III-nitrides

1.1 Crystal Structure

The group III-nitride material system is composed of the group III compounds aluminum (Al), gallium (Ga), indium (In) and nitrogen (N) as well as their alloys. The group III compounds form a wurtzite (hexagonal) (α-phase) or zinc blende (cubic) (β-phase) structure. Under ambient conditions, wurtzite is the most thermodynamically stable structure for bulk aluminum nitride (AlN), gallium nitride (GaN) and indium nitride (InN).

In Fig. 1-1, a tetrahedral arrangement of atoms is presented showing the wurtzite (hexagonal) crystal structure, with lattice constants a and c, formed by two interpenetrating hexagonal closed packed (hcp) sublattices, each with one type of atom, offset by \( \frac{5c}{8} \) along c-axis. The space group for wurtzite structure is \( P6_3mc \) in the Hermann-Mauguin notation and \( C_{4h} \) in the Schoenflies notation system. The wurtzitic polytype consists of 6 atoms of each type with each one of the atoms, e.g. the Nitrogen atom being tetrahedrally coordinated. The stacking sequence for the (0001) closed-packed planes is AaBbCcAaCcBb (using uppercase and lowercase letters denoting the two planes). Furthermore, another stacking sequence of biatomic close-packed (0001) planes of Ga and N pairs is well known: the AaBbAb [1], [2].

![Fig. 1-1: (a) Wurtzite crystal structure unit cell (dashed line). It consists of two interdependent hexagonal closed packed sublattices, displaced by 5/8 on c (0001) axis, (b) Stacking sequence of wurtzite <0001> polytypes [2].](image)

The space group concerning the zincblende structure is \( F\overline{4}3m \) in the Hermann-Mauguin and \( T_d^2 \) in the Schoenflies notation systems. In the zincblende structure, a cubic unit cell exists, which contains four group III elements and four nitrogen elements, positioned identically as in the diamond crystal structure. In this system, two interpenetrating face centered cubic sublattices, offset by \( \frac{1}{4} \) of the distance along a body diagonal, with a tetrahedral arrangement of atoms (Fig. 1-2). The stacking sequence is AaBbCc for the (111) closed-packed planes (using uppercase and lowercase letters denoting the two planes) [1].
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Fig. 1-2: (a) Zincblende crystal structure unit cell. It consists of two interpenetrating face centered cubic sublattices, displaced by 1/4 of the distance along a body diagonal, (b) Stacking sequence of zinc blende <11\overline{1}> polytypes [2].

Generally, the wurtzite and zinc blende crystal structures are quite similar. In both cases, each atom is coordinated by four nitrogen atoms and vice versa. However, the main difference concerns the stacking sequence of close-packed planes. The coexistence of hexagonal and cubic phases is possible in epitaxial layers, for example due to stacking faults [3]. Fig. 1-3 shows a tetrahedron, presenting the tetrahedral bonding between the two elements (e.g. Ga and N). It is easy to notice that the atom No1 (e.g. Ga atom) is at the centroid (dividing the height in a ratio of 3:1) of four No2 atoms (e.g. N atoms) or vice versa and it is bonded to each of these atoms by a partly ionic partly covalent bond. One of the four bonds is parallel to c-axis (in our case the vertical bond). The triangular tetrahedron base defines a c-plane and the interlayer distance $d_{0001}$ equals to the tetrahedron height.

The tetrahedron can occupy one of the three sites on a c-plane: T_1, T_2 and T_3. These tetrahedra, after being rotated by 180° around c-axis, become the twinned variants T'_1, T'_2 and T'_3. Fig. 1-4 shows the projection of the tetrahedral in a {11\overline{2}0} plane as well as the projection of the three possible sites occupied by the tetrahedral. If we represent the Ga with white colored circles and the N with black colored circles in Fig. 1-4, it is clear that the Ga sheet of atoms is located parallel and above the N sheet of atoms at a distance of $\frac{3}{4}d_{0001}$. The Ga and N atoms in the double sheet are denoted by Roman (A, B, C) and Greek (α, β, γ) letters or vice versa. Thus, for example, tetrahedron T_1 is associated with a αA double sheet of atoms passing through the centroid and the vertex of the tetrahedron [4].
The III-N compound semiconductors crystal structure (both wurtzite and zincblende) lacks of an inversion center, exhibiting polar axis: it is non-centrosymmetric. In particular, the bonds in the \( \langle 0001 \rangle \) direction for wurtzite and \( \langle 111 \rangle \) direction for zincblende are all faced by nitrogen in the same direction and by the cation in the opposite.

As explained in detail later, due to this lack of inversion symmetry, a large polarization charge (sheet charge of opposite polarity) will build up on two surfaces (top surface and basal surface) in GaN like materials. This polarization charge is very large (generally \( >10^{13} \text{ cm}^{-2} \)) which leads to very high electric field (~ in MV) in III-N materials [5]. Moreover, both bulk and surface properties can depend significantly on whether the surface is faced by nitrogen or metal atoms [3].

### 1.2 III-nitrides properties

III-nitrides semiconductors (AlN, GaN and InN) have a big potential to be used in optoelectronic devices (as emitters and detectors) and also at high power/temperature electronic devices [6]. The group III-nitrides as well as their ternary and quaternary alloys show a number of very attractive physical, optical and electronic properties, resulting in novel materials and device structures. As already mentioned, group III-nitrides can present a hexagonal (wurtzite) or a cubic (zincblende) crystal structure, with the hexagonal being the most stable one.

The hexagonal crystal structure of III-nitrides can be described by the edge length \( a_0 \) of the basal hexagon, the height \( c_0 \) of the hexagonal prism and finally an internal parameter \( u \) defined as the anion-cation bond length along \( \langle 0001 \rangle \) axis. The ionic radii for Al, Ga and In is: \( \text{Al}^{3+}: 0.39 \text{ Å}, \text{Ga}^{3+}: 0.47 \text{ Å}, \text{In}^{3+}: 0.79 \text{ Å} \) respectively [3].

The strong ionic III-N bonds result in the distortion of the unit cell from the ideal wurtzite unit cell, causing a large spontaneous polarization along \( c \)-axis. Due to the large differences
between the ionic radii and bonding energies of the group III metal cations, different lattice constants and band-gap energies exist, and so the epitaxial deposition of these materials is a challenge. Fig. 1-5 shows the lattice constants and bandgap energies for wurtzite and zinc blende group III-nitride materials, also including the commonly used substrates for the growth of epilayers. The materials properties for GaN, AlN and InN are presented in Table 1-1 [7]–[10].

The lattice mismatch between III-nitride materials and the most commonly used substrates results in a high dislocation density, affecting the mechanical and optoelectronic properties in the epilayers as well as the surface morphology of epilayers.

<table>
<thead>
<tr>
<th>Crystalline properties</th>
<th>Index</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.11</td>
<td>3.19</td>
<td>3.54</td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>4.98</td>
<td>5.19</td>
<td>5.70</td>
<td></td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (10^6/°C)</td>
<td>4.20</td>
<td>5.59</td>
<td>5.70</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity (W/(cm·K))</td>
<td>2.85</td>
<td>2.1</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>&gt;3000</td>
<td>&gt;2500</td>
<td>&gt;1100</td>
<td></td>
</tr>
<tr>
<td>Bulk modulus (GPa) (300K)</td>
<td>210</td>
<td>210±10</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Bond length (Å)</td>
<td>1.89</td>
<td>1.94</td>
<td>2.15</td>
<td></td>
</tr>
<tr>
<td>Energy gap (eV)</td>
<td>6.2</td>
<td>3.39</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Electron mobility (cm²·V⁻¹·s⁻¹)</td>
<td>300 (Theor.)</td>
<td>1000 (Theor.)</td>
<td>14000 (Theor.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>426 (Expt.)</td>
<td>900 (Expt.)</td>
<td>3980 (Expt.)</td>
<td></td>
</tr>
<tr>
<td>Basal (1100)</td>
<td>2.490</td>
<td>2.595</td>
<td>2.850</td>
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<tr>
<td>Interplanar separations</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(1120)</td>
<td>2.693</td>
<td>2.762</td>
<td>3.066</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.556</td>
<td>1.595</td>
<td>1.772</td>
<td></td>
</tr>
</tbody>
</table>

Table 1-1: Materials properties for wurtzite III-nitrides.
Hexagonal boron nitride (h-BN) is recently being used (at package-level) for the local thermal management in high-power transistors suffering from inefficient heat dissipation of the hotspots, which elevate the local temperature and significantly degrade the performance and reliability of the device. Thus, by using thermally conductive and electrical insulating few-layer hexagonal boron nitride (h-BN) as heat spreaders and thick counterpart as heat sinks the temperature decreases and an improvement of saturation current, cut-off frequency and maximum oscillation frequency has been reported [11], [12].

The evolution of the bandgap values and band alignments for the binaries InN, AlN and GaN and also their ternaries is depicted in Fig. 1-6. It is clearly seen that the energy bandgap ranges from 6.1 eV (AlN case) to 0.7 eV (InN case). Moreover, the ternaries energy gap maybe easily engineered over a wide range, utilizing this feature in many applications [13].

![Valence band position and offsets for group III-nitrides alloys.](image)

It is important to focus on the GaN properties, the most studied one among III-nitrides materials. First of all, its wide band gap makes it an excellent candidate for high temperature device operation. It is important to mention that GaN is in most cases the starting material during heterostructure epitaxy, with the most commonly used growth direction normal to (0001) basal plane (as already mentioned the atoms are arranged in bilayers of two closely spaced hexagonal layers, the one with cations and the other with anions, so that the bilayers have polar faces).

Furthermore, GaN exhibits very interesting electrical properties. The high thermal conductivity (ten times higher than GaAs) and high breakdown fields (3x10^6 V·cm⁻¹) processes make it an excellent and very promising candidate for use in high power and high temperature applications. GaN also features very attractive transport properties as well as high peak velocity (close to 3x10^7 cm/s) and high saturation velocity (about 2.6x10^7 cm/s), with values remarkably higher than the values for Si and GaAs. However, the major obstacle of
GaN growth concerns the lack of a suitable lattice matched and thermally compatible substrate material [6].

### 1.3 Polarization effects of Nitrides

The crystal surface of GaN can have either Ga-polarity (Ga atoms on the top of the \( \{0001\} \) bilayer, corresponding to \( [0001] \) polarity) or N-polarity (N atoms on the top of the \( \{0001\} \) bilayer, corresponding to \( [000\bar{1}] \) polarity), depending on the layer on which the GaN crystal is grown (as explained further in the next paragraphs). It is important to make clear that Ga-faced does not mean Ga-terminated (termination is used only to describe a surface property). Thus, a Ga-faced material can be Ga or N-terminated. GaN polarity is determined by substrate polarity (if grown directly on a substrate), nucleation layer (if grown on a nucleation layer) and by the growth method. Polarity plays a crucial role on the defect formation and thus on the device performance [3], [14]. Different polarity results in different physical and chemical properties of the structures.

The wurtzite group III nitrides exhibit two different kinds of polarization, the piezoelectric and the spontaneous, whereas the zincblende exhibits only piezoelectric polarization.

#### 1.3.1 Piezoelectric polarization

The piezoelectric effect is merely restricted to non-centrosymmetric crystals (as zincblende and wurtzite systems). Generally, crystals that present an inversion symmetry in their structure, when elastically strained, they become electrically polarized. This phenomenon is known as piezoelectricity. More specifically, lattice deformation induces a separation of centers of positive and negative charges in the crystals thus forming dipole moments, the accumulation of which gives rise to polar charges on the crystal surface [15]. The cause of this strain in the heterostructures is the lattice constant and the thermal expansion coefficient difference.

As III-nitrides, GaN and AlGaN materials exhibit strong piezoelectric effects. When high voltage is applied, large stress is induced in these materials (inverse piezoelectric effect). In a High Electron Mobility Transistor (HEMT) structure, where III-nitrides are used, when operating in high voltages, a large electric field is present under the gate edge across the barrier. This fact results in a large mechanical stress concentrated in a very small region in the AlGaN layer. Moreover, because of the lattice mismatch, when grown AlGaN on GaN layer, tensile strain exists and elastic energy is stored at rest, forming crystallographic defects when exceeding a critical value [16].

The piezoelectric polarization depends on the amount of strain. For larger amounts of strain, a larger piezoelectric polarization is observed. Moreover, compressive strain results to an opposite orientation polarization compared to the tensile strain.
1.3.2 Spontaneous polarization

On the other hand, even if strain is not present, another type of polarization is shown, called spontaneous polarization. This type of polarization is caused by the lower symmetry of the wurtzite structure, due to the fact that there is a huge difference in electronegativity between group III metals and the N atom, resulting in a highly ionic III-N bond.

According to the point group symmetry, both zincblende and wurtzite are non-centrosymmetrical. The wurtzite structure, with its unique 6-fold symmetry axis and mirror planes containing it, can show a spontaneous polarization parallel to the polar axis (c-axis). However, zincblende structure presents four polar three-fold rotation axis (the [111] equivalent direction) but also possesses four-fold inversion axis (the [001] equivalent directions) (Fig. 1-7). Thus a spontaneous polarization cannot occur in zincblende structures.

![Fig. 1-7: Cubic zincblende and hexagonal wurtzite-type of structure. Sum of the microscopic dipoles results in zero spontaneous polarization (zincblende structure) and in non-zero spontaneous polarization (wurtzite structure).](image)

1.3.3 Total polarization

The total crystal polarization is given by the following equation:

\[ P_{\text{total}} = P_{\text{sp}} + P_{\text{pz}} \]  \hspace{1cm} (1-1) 

where \( P_{\text{sp}} \) is the spontaneous and \( P_{\text{pz}} \) the piezoelectric polarization.

Generally, for nitride semiconductors, the \((0001)\) (Ga polar) and \((000\overline{1})\) (N polar) planes are referred to as the c-plane. The nitride epitaxial films are polar materials if the film surface is c-plane. Either wise, if the surface is the \(\{1\overline{1}00\}\) plane (m-plane) or the \(\{1\overline{1}20\}\) plane (a-plane), parallel to the polar axis (c-axis), no polarization effect occurs along the growth direction and the nitride is nonpolar. If the film surface is neither parallel nor normal to the c-axis, the material is semipolar (as for example the \(\{1\overline{1}02\}\) plane (r-plane)). A schematic drawing of the commonly used surface orientations for GaN grown material and heterostructures is shown in Fig. 1-8 [17].

Polarization induces tilted energy bands in polar nitrides, favor of the formation of a high-density 2DEG (2-Dimensional Electron Gas) in electronic devices [15]. However, in other
electronic devices such as LEDs (Light-Emitting Diodes), the polarization effects create built-in electric fields resulting to quantum-confined Stark effects (QCSEs) [18].

![Schematic drawing of the commonly used surface orientations. Gallium atoms are represented by yellow (larger) balls whereas the nitrogen atoms by blue (smaller). Thin solid lines indicate the bonds. The different orientations are: the polar (a) c-plane, the nonpolar (b) m{1100} and (c) a{1120} planes, and the semipolar (d) {1101} and (e) {1122} planes [17].](image)

**Fig. 1-8:** Schematic drawing of the commonly used surface orientations. Gallium atoms are represented by yellow (larger) balls whereas the nitrogen atoms by blue (smaller). Thin solid lines indicate the bonds. The different orientations are: the polar (a) c-plane, the nonpolar (b) m{1100} and (c) a{1120} planes, and the semipolar (d) {1101} and (e) {1122} planes [17].

The spontaneous polarization $P_{sp}$ of the group III-nitrides was calculated by F. Bernardini and V. Fiorentini [19]: -0.081 (C/m$^2$) for AlN, -0.029 (C/m$^2$) for GaN and finally -0.032 (C/m$^2$) for InN, as shown in detail in Fig. 1-9. Theoretical calculations have thus indicated that for GaN, AlN and InN nitrides the spontaneous polarization field is towards the [0001] direction, pointing from the A (Ga) face to B (N) face, as shown in Fig. 1-10. For piezoelectric polarization, for (0001) films grown under tensile strain the signs of the relevant piezoelectric coefficients are such that $P_{pz}$ points to [0001] and under compressive strain the signs of the relevant piezoelectric coefficients are such that $P_{pz}$ points to [0001] [20].

![Spontaneous (indicated with filled red circles) and piezoelectric (indicated with open blue squares) polarization for the III-N compounds [12].](image)

**Fig. 1-9:** Spontaneous (indicated with filled red circles) and piezoelectric (indicated with open blue squares) polarization for the III-N compounds [12].

![Crystal structure and spontaneous polarization field for GaN [20].](image)

**Fig. 1-10:** Crystal structure and spontaneous polarization field for GaN [20].

For example, when GaN is grown on a substrate, in Ga-face situation, the crystallographic c-axis and the internal electric field (through piezoelectric polarization) point away from the substrate towards the surface, whereas the spontaneous polarization has the opposite direction.
The polarization-induced fixed lattice charges are negative at the surface and positive at the substrate interface. For N-face material, all charges and directions are inverted. As indicated in Fig. 1-11, both Ga and N-face regions can co-exist, forming inversion domain boundaries (IDB), separating adjacent domains with opposite polarity [21].

As already indicated, GaN is a strongly polar material and it shows a spontaneous polarization resulting in sheet charge accumulation in the end regions of the crystal, of the same magnitude but opposite sign, for keeping charge neutrality.

Similarly, AlGaN is also a polar material, depending on the Al content. Moreover, because of the difference in the lattice constant between AlGaN and GaN, a piezoelectric polarization is present in the heterointerface. So, in the AlGaN/GaN interface, there exists a difference in the polarization vector and the polarization fields are very strong, providing with electrons the High Electron Mobility Transistor (HEMT) channel, as explained in detail later. In the AlGaN/GaN heterostructures, the spontaneous is larger than the piezoelectric polarization. But, in any case, we have to take them into consideration, since both of them strongly affect the HEMT potential profile.

Let’s consider the AlGaN/GaN heterojunction illustration of Fig. 1-12 with polarization fields along growth direction (c-axis [0001]).
The piezoelectric polarization is negative for tensile and positive for compressive strain [20]. The direction of the spontaneous polarization field depends on the fact whether the AlGaN surface is cation or anion terminated. For Ga (Al)-face heterostructures, the spontaneous polarization is negative with a direction showing towards the substrate [22]. According to these, in the case of a tensile strain, the spontaneous and piezoelectric polarizations orientations are parallel, as shown in Fig. 1-12 (b) and (c) for Ga- and N-face structures respectively. Moreover, due to the fact that the spontaneous polarization magnitude of GaN and AlGaN are different, there exists a polarization discontinuity in the interface resulting in an interface charge, with the sheet charge density proportional to the polarization difference. More specifically, in Fig. 1-12, in the case that AlGaN is grown on the top of a GaN layer, a tensile strain situation exists and the sheet charge density is positive, attracting electrons:

\[ P_{total} = (P_{sp} + P_{pz})_{AlGaN} - (P_{sp})_{GaN} > 0 \]  

In previous studies, it has been shown that piezoelectric fields in strained pseudomorphic group-III-nitride heterostructures, e.g. AlGaN grown on thick GaN layer with [0001] growth direction, resulted to an increased incorporation of donor effects in AlGaN, enhancing the charge transfer to GaN layer [23].

The piezoelectric polarization of a material exists under complete strain. In the case of a strain relaxation being induced, the piezoelectric effect is weakened. According to the elastic strain relaxation theory, the relaxation degree of the Al\(_x\)Ga\(_{1-x}\)N internal stress is a function of \(x\) and the alloy layer thickness \(d\). Moreover, even in the case of relaxed materials, because of the difference in spontaneous polarizations between AlGaN and GaN, there exists a positive
charge density in the interface, attracting and confining electrons in very thin region. However, in the case of interdiffusion within a relatively large range of thickness in the heterointerfaces, the gradient of spontaneous polarization is also reduced, showing a weaker polarization effect. Finally, in mixed polarity case, where a random distribution of polarity inversion domains exists, the total polarization effect may disappear [15].

1.5 Lattice polarity setting

There are two ways in order to affect/determine the polarity of a material. First of all, it can be accomplished with use of the two sides of opposite polarity of a free-standing III-nitride specimen e.g. obtained by high pressure–high temperature synthesis or by laser-induced lift-off from a hetero-substrate. Moreover, a second way concerns the use of polar substrates (e.g. SiC), prepared as bulk crystals with predefined polarity. In this way, we can therefore affect and set the polarity of the heteroepitaxially grown layers. In the example that follows, high quality III-nitrides, grown by MOCVD on sapphire show a Ga-face polarity (while similar grown with MBE show N-face polarity) [21]. This situation is illustrated in Fig. 1-13, where a GaN grown by MBE can exhibit N-face polarity (if grown on the top of the sapphire substrate), or a Ga-face polarity (if an AlN buffer layer is deposited in between). Usually, sapphire substrates are Oxygen-terminated, with this termination being stable against nitridation for a considerable amount of time (hours). It is therefore reasonable that the first monolayer of the deposited material must have Ga (for the first case on the left of Fig. 1-13) or Al (for the second case on the right of Fig. 1-13).

![Fig. 1-13: Schematic view of the III-nitride/sapphire interface with (right part) or without (left part) an AlN buffer layer [21].](image)

The difference between these two cases derives from the different chemical strength of the II–N versus the III–O bonds. Since Ga–N is stronger than Ga–O bonding, the first Ga monolayer deposited on the substrate belongs to the GaN epilayer, which consequently shows N-face polarity (left part of Fig. 1-13). On the other hand, if Al is deposited on substrate, the first metal monolayer still belongs to the substrate, because Al–O bonding is stronger than
Al–N bonds. Instead, the subsequently deposited N-layer is the first monolayer belonging to the growing III-nitride crystal, which, therefore, now has the opposite polarity (Al-face or Ga-face). Thus, the polarity can be easily inverted by depositing a thin AlN buffer layer at the beginning of MBE growth [21] or MOVPE growth [24].

1.6 Epitaxy

The term “epitaxy" derives from the Greek word “επίταξη”, with the “epi” meaning “on” and “taxy” meaning “arrangement”. Epitaxial growth refers to the deposition of thin, single layers onto a suitable substrate on which they grow in the form of crystals. Homoepitaxy growth is called the epitaxy of the same as the substrate material. Otherwise is called heteroepitaxy. The epitaxial layer adopts a specific lattice structure and orientation with respect to the substrate grown on [25].

1.6.1 Step controlled epitaxy

Conventional epitaxial growth uses a deposition flux from gaseous or liquid precursors. The deposition atoms, when being absorbed on a substrate, they become adatoms, diffusing on the substrate surface. Several adatoms can meet each other and form a stable island (two-dimensional nucleation). Other adatoms may come to join the existing islands or be adsorbed by the substrate steps and defects where more dangling bonds are present. In the case of many islands grown on the substrate, there will be competition for adatoms between adjacent islands. The islands continue to grow until they coalesce to even larger islands, which finally cover the whole substrate surface.

If the growth takes place mainly at the surface steps, two important phenomena occur known as “step-flow" and “step-bunching”. When using high temperature growth conditions, the diffusion length (average distance that chemical species migrate on a step-free surface before desorption) of adatoms is greater than the terrace width and so the adatoms are incorporated at the step edges without forming islands on the terrace. The incorporation of adatoms causes the steps to advance along the interface (Figure 1-14 (a)), phenomenon known as step-flow growth. However, if the adatom absorption capability for adjacent steps is not the same, these steps may advance at different velocities. Eventually, they may bunch together to form a larger step, in a phenomenon referred to as step bunching, as presented in Fig. 1-14 (b) [25]. Generally, when a heteroepitaxial film is grown on a vicinal substrate, the terrace steps at the growth front may bunch together in order to relieve strain, resulting in a rough surface [26].

Furthermore, besides growth conditions (as temperature), the substrate off-cut angle plays an important role in the growth mode of the epilayer. As shown in Fig. 1-15, in the growth on a (0001) Si-terminated SiC substrate case, the adatoms can be incorporated at two possible sites on the terrace and at a unique occupation site at a step. On on-axis faces, the step density
is low and thus wide terraces exist on the substrate surface. In CVD, the adsorbed chemical species energy is very low in order to reach steps (at a low temperature of 1500°C), due to the fact that the terraces are wide enough. Thus, growth occurs mostly on terraces with the formation of two-dimensional islands. For example, 3C-SiC can be grown on a 6H-SiC substrate through two-dimensional nucleation. The polytype of the overgrown layers is determined by the growth conditions (mainly temperature). On the other hand, on off-axis faces, the step density is rather high, resulting to narrow width terraces and so it is easy for the adsorbed species to reach steps positions, even when using low temperature growth conditions (1500°C). At a step, step bonds uniquely determine the incorporation site. In this way, the steps serve as a template that results in the replication of the stacking order of the substrate, in homoepitaxy. Finally, the parameter determining whether the growth mode is step-flow or two-dimensional nucleation, is the supersaturation ratio \( a \) (the ratio of the number of chemical species per unit area on the surface to the equilibrium value).

If \( a_{\text{max}}>a_{\text{crit}} \) step-flow and if \( a_{\text{max}}>a_{\text{crit}} \) two-dimensional nucleation [27].

Fig. 1-14: (a) Step-flow growth, (b) Step-bunching.

Fig. 1-15: Surface illustration of 6H-SiC having vast terraces and a low density of steps, with the possible incorporation sites indicated with arrows.

1.7 Epitaxial growth techniques

Several methods have been developed for the epitaxial grown of group III-nitrides materials. The most important parameter to be achieved during growth procedure is high crystalline quality surfaces and interfaces of epilayers. Metalorganic chemical vapor
deposition (MOCVD) is the most commonly used growth method. For that reason, a more extensive description of this method follows in the next paragraphs.

MOCVD is a technique that is used for the deposition of very thin layers of atoms onto a semiconductor wafer. It is the most significant manufacturing process for III-V compound semiconductors, especially for those based on Gallium Nitride (GaN). These semiconductors are the most important base material for manufacturing red, blue, green and white LEDs. MOCVD is also known as: MOVPE (metal organic vapor phase epitaxy), OMVPE (organo-metallic vapor phase epitaxy) and OMCVD (organo-metallic chemical vapor deposition).

To produce compound semiconductors, the chemicals are vaporized and transported into the reactor together with other gases. There, the critical chemical reaction takes place that turns the chemicals into the desired crystal (the compound semiconductor). In MOCVD the injected gases are ultra-pure and can be finely dosed. The chemicals used for the deposition process are atoms of group III such as Ga, In, Al, combined with complex organic gas molecules, and atoms of group V such as As, P, N, combined with hydrogen atoms [28].

The MOVPE growth process reactions taking place are shown schematically in Fig. 1-16. The substrate lays on a graphite susceptor heated by IR-lamps (Fig. 1-17). Due to this heat the gas molecules, which are flowing above the susceptor, are decomposed and the pure elements are incorporated into the substrate, whereas the methyl and ethyl groups desorb and are pumped away [29]. The surface reactions occurring during MOCVD growth include adsorption and desorption of the precursor molecules, surface diffusion, nucleation and growth, and desorption of reaction products. Fig. 1-17 presents the planetary reactor technology used by Aixtron, based in horizontal laminar glow. The required gases enter the deposition chamber through a gas inlet (or nozzle) located in the center of the reactor ceiling.

![Fig. 1-16: Schematic illustration of the surface reactions taking place during MOCVD procedure.](image)

![Fig. 1-17: The planetary Reactor technology provided by Aixtron [28].](image)

After the MOCVD deposition process, the different crystal structures are processed into numerous different electronic or optoelectronic devices, such as LEDs, lasers, transistors and solar cells.

Other methods used for the III group-Nitrides growth include among others the Hydride Vapor Phase Epitaxy (HVPE) method, the Molecular Beam Epitaxy (MBE) and plasma-
assisted MBE method, the Remote-plasma-enhanced or reactive RF-sputtering CVD method, etc.

1.8 Substrates for nitride epitaxy

The substrate used for nitride epitaxy is a very important factor determining the crystal orientation, the polytype, the polarity, the surface morphology, the strain existence as well as the defect concentration of the nitride epilayers overgrown. Thus, the substrate properties may ultimately affect and determine the device performance. However, one of the main problems for nitride growth is the lack of a lattice-matched and thermally compatible substrate material. For the growth of these materials, different substrates have been used. These include sapphire, SiC and silicon.

Sapphire is a commonly used substrate for GaN epitaxy [30], [31]. This kind of substrate is quite inexpensive and can be widely commercially found with diameters up to 6 inches. However, the large lattice mismatch with GaN (+16%) results to high dislocation densities in the GaN epilayer, causing reduced carrier mobility and thus degrading device performance. Moreover, sapphire shows a 34% greater CTE as compared to GaN, resulting in biaxial compressive stress in the epilayer when cooling down after deposition. It is also possible for the film and substrate to crack, when exceeding a critical thickness [32]. Furthermore, sapphire exhibits a low thermal conductivity (0.3 W/cm·K), not being therefore suitable for power applications.

On the other hand, SiC is more expensive than sapphire but it provides more desirable properties such as heat transport and decreased lattice mismatch (+3.5% for (0001) 6H-SiC). The basic structure for all 250 polytypes it shows is a tetrahedron of C atoms covalently bonded with a Si atom at its center, or vice versa. The most common SiC polytypes used for GaN epitaxy are 4H-SiC and 6H-SiC (wurtzite structures). Another important characteristic is the high thermal conductivity (4.2 W/cm·K). SiC exhibits a lower CTE as compared to GaN, resulting in biaxial tension applied in films at room temperature. Possible applications of nitrides grown on SiC include blue-green LEDs, blue lasers, UV emitters as well as HEMTs.

Moreover, silicon (exhibiting a cubic structure) is a very good and inexpensive opportunity to incorporate the group III-nitrides into the well-established silicon technology. Another advantage of using silicon substrates is the availability of large substrates, as well as its crystal quality and thermal stability. However, its large lattice (-17%) and CTE (+54%) mismatch with GaN together with the tendency to form an amorphous silicon nitride layer result in much poorer GaN epilayers as compared to the other substrates. Possible applications of nitrides grown on Si (111) include HEMTs, blue LEDs as well as Schottky-barrier ultraviolet detectors [3].

All the above substrates show thermal and lattice mismatches to AlN, GaN and InN resulting in strain issues. However, it is widely believed and proved that the homoepitaxial growth of group III-nitrides in native substrates would result in the highest quality epilayers. However, these bulk native substrates are very expensive and also unavailable [3], [13], [33]. Indeed, the best substrate choice for GaN epitaxy is gallium nitride itself. The use of GaN
substrate results in annihilation of heteroepitaxy related issues. GaN homoepitaxy provides good polarity control and dopant concentration, and results to low stress, thermal expansion coefficient (CTE) and lattice constant mismatch. Therefore, the use of interlayers for stress reduction and lattice mismatch issues is limited (interlayers are used in heteroepitaxy on silicon, sapphire or silicon carbide substrates). However, the disadvantage concerns the fact that GaN is still not available in large diameter wafers and also the price of fabrication of free standing GaN is very high [6].

Thus, foreign substrates are mostly used for the grown of the group III-nitrides, dealing with issues as different lattice parameters and thermal expansion coefficients, resulting in strain phenomena. However, properties other than lattice constants and thermal compatibility are also important, including the crystal structure, surface termination, composition, chemical and electrical properties etc. Table 1-2 [7]–[10], [34], [35] presents the properties of the most often used substrates for epitaxial growth.

<table>
<thead>
<tr>
<th>Crystalline properties</th>
<th>Index</th>
<th>AIN</th>
<th>GaN</th>
<th>6H-SiC</th>
<th>4H-SiC</th>
<th>Si(111)</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.11</td>
<td>3.189</td>
<td>3.08</td>
<td>3.073</td>
<td>5.43</td>
<td>4.758</td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>4.98</td>
<td>5.186</td>
<td>15.12</td>
<td>10.053</td>
<td>-</td>
<td>12.991</td>
<td></td>
</tr>
<tr>
<td><strong>Thermal Expansion Coefficient (10⁴/K)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å) (in plane)</td>
<td>4.2</td>
<td>5.59</td>
<td>4.2</td>
<td>2.59</td>
<td>7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.3</td>
<td>3.17</td>
<td>4.68</td>
<td>-</td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Thermal Conductivity (W/(cm·K))</strong></td>
<td>2.85</td>
<td>2.1</td>
<td>4.2</td>
<td>3.7</td>
<td>1.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td><strong>Lattice mismatch GaN/substrate</strong></td>
<td>+2.4%</td>
<td>-</td>
<td>+3.5%</td>
<td>-16.9%</td>
<td>+16%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Thermal mismatch GaN/substrate</strong></td>
<td>+25%</td>
<td>-</td>
<td>+25%</td>
<td>+54%</td>
<td>-34%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1-2: Physical properties of the GaN, AIN, 6H-SiC, Al₂O₃, Si (111). The given thermal expansion coefficient is an averaged value and might differ significantly at very low and at high temperatures.

1.9 Defects/cracks formation-issues in nitride epilayers

Defects in crystalline solid are imperfections in the atoms arrangements, with negative impact on the device performance, including point, linear, planar and volume types.

Basal-plane stacking faults (BSFs) are planar defects that interrupt the stacking sequence along [0001] axis [36], by introducing one or more planes to the stacking rules. The types of BSFs are: intrinsic (type-I and type-II) and extrinsic. Stacking faults are electrically detrimental defects, so ways for their reduction are worldwide searched [37].

Due to the lattice mismatch between the substrate and the films grown on, strain is induced. The elastic strain energy increases with the film thickness. Thus, there is a critical thickness that is energetically favorable to introduce misfit dislocations at the interface. Dislocations represent a one-dimensional line defect that typically exists in very high densities in nitrides-based devices, far higher than in other semiconductor devices. These are
associated with a wide range of undesirable properties such as reduced efficiencies and lifetime, working as electron traps in the epilayers. According to Marino F. [38], GaN HEMT performance exhibits a fairly large dependence on the density of threading dislocation (TD) defects. Furthermore, they reported that threshold concentration exists, above which a complete degradation of the device operation occurs. While dislocations have been extensively studied, they are still not well understood especially in regards to how they interact with other species—such as native point defects, impurities, dopant atoms and alloying additions [39].

Generally, they are characterized by the Burger vector \( \vec{b} \) and dislocation line \( \vec{u} \). Concerning hexagonal materials, there are three types of dislocations: a type (edge dislocations) with \( \vec{b} = \frac{1}{3} < 1 \bar{1} 2 0 > \), c type (screw dislocations) with \( \vec{b} = < 0 0 0 1 > \), and a+c type with \( \vec{b} = \frac{1}{3} < 1 \bar{1} 2 3 > \). Experimentally, it is known that the line directions of the majority of TDs are normal to the film/substrate interface and parallel to the [0001] direction. Moreover, the majority of TDs are edge type dislocations. Mixed dislocations are inclined at approximately 12 deg to the film normal [40]. Additionally, it appears that the edge character dislocations represent a larger fraction of the total TD density in thicker films [41]. Pure screw dislocations are the uncommon type of TD in GaN films (10% of the overall TD density in MOCVD-grown material) [42]. Moreover, Wu et al. [41] reported that pure screw TDs represent a very small proportion (less than 1%) of the total TD density in the MOCVD-grown GaN material.

Despite the fact that a high enough lattice mismatch results in a high dislocation density in the GaN layers, the major problem seeking for solutions is the large thermal mismatch of most compound semiconductors and Si. Due to the large thermal mismatch, it is difficult to achieve device-relevant layer thicknesses and cracking is observed [8].

Below, some of the most common issues when growing nitrides on Si/Sapphire/SiC substrates are referred:

A well-known issue of MOVPE grown GaN on Si is referred as melt-back etching effect. According to this effect, when using elevated temperatures, Ga and Si form an alloy. This alloy begins a fast etching reaction and finally it destroys the layer and the substrate. Moreover, a very important problem that GaN layers grown on Si (111) deal with are the cracks when exceeding about 1 \( \mu \)m in thickness [43]. Typical ways to confront this issue and achieve high-quality GaN layers concerns strain engineering, by patterning the substrate with masking or etching the substrate or a buffer layer, by using AlGaN buffer layers on AlN seed layers, by using AlGaN/GaN multilayers (reducing dislocations and inducing a compressive strain in the layers overgrown) or finally by introducing Low Temperature (LT) AlN interlayers [44]. This does not only apply to light emitters where thick layers are required to achieve good electrical and structural properties, but it is also required for transistor structures [8].

Concerning nitride growth on SiC/Sapphire substrates, for example, because of the very large (+16%) lattice mismatch of GaN/Sapphire, the growth of individual and isolated islands
takes place, instead of a continuous film. Usually, dislocations of high density of edge, screw and mixed type are formed when epilayers are grown directly on the substrates. Moreover, the poor wetting of GaN on 6H-SiC (0001) substrates has been referred, preventing direct nucleation and resulting in poor quality films [45]. In order to improve the epilayers quality, buffer layers are introduced prior to the epilayer growth, providing nucleation centers with the same orientation with the substrate, promoting lateral growth and accommodating partly the strain. Moreover, buffer layers result in the improvement of the surface morphology, the structural and optical properties, the reduction of dislocations, the elimination of the columnar interfacial growth as well as the increase of the critical for cracking thickness [46]. More specifically, AlN or Al$_x$Ga$_{1-x}$N buffer layers are grown directly on SiC/Sapphire substrates, template suitable for the subsequent GaN epilayers growth [47], [48].

### 1.9.1 Defect reduction strategies

Because of the large number of slightly misoriented and coalescing grains, the film must necessarily contain a high density of grain boundaries and also threading dislocations. For the defects reduction, a variety of different processes were proposed. Each one of them uses one of the three basic strategies: the improvement of grain alignment, the increase of grain size and the filtering of threading dislocations. Thus, by improving the grain alignment, the dislocations density is reduced. By growing larger grain size epilayers, the dislocations density is also reduced as it reduces the grain boundaries number. Finally, by using dislocation filtering methods (e.g. engineered layers for the dislocation recombination enhancement), the dislocations either recombine or annihilate, as moving towards the structure surface [49].

The strategy of growing larger grain structures can be divided into two different approaches: the optimal pressure growth (OPG) and the lateral epitaxial overgrowth (ELO). However, both of them control the grain nucleation at the onset of HT growth, so that a lower density of grains succeeds in nucleating. This is managed either by controlling growth parameters (in OPG) or by permitting nucleation only in specific substrate regions (in ELO) [49].
Chapter 2: High Electron Mobility Transistor

2.1 Operation principle-Structure

The transistor, the fundamental building block for electronics, is a semiconductor device used to control or amplify electronic signals and electrical power. The transistor is comprised of three terminals for its connection to an external circuit: the collector, the base and the emitter. Generally, there are two basic categories of transistors: the bipolar junction transistor (BJT) and the field effect transistor (FET). The High Electron Mobility Transistor (HEMT), also known as heterostructure FET (HFET), is a field effect transistor, containing a junction between two different band gap materials, forming the heterostructure. The modern epitaxy techniques used for high quality semiconductor layers growth, enable the growth of very fast and low noise HEMTs, for high frequency application (20-100 GHz) [3].

The invention of the HEMT is usually attributed to Takashi Mimura (Fujitsu, Japan). In America, Ray Dingle and his co-workers in Bell Laboratories also played an important role in the invention of the HEMT. A HEMT component uses three contacts: the drain, the source and the gate. A cross section of the HEMT structure is shown in Fig. 2-1. In HEMTs, the current flow between two ohmic contacts, source and drain, is controlled by a third contact, the gate. Most often the gate is a Schottky contact [50]. The basic principle of its operation is very similar to those of the metal–semiconductor field-effect transistor (MESFET). The basic difference between the two concerns the layers structure.

![Fig. 2-1: Typical GaN HEMT structure.](image)

In conventional transistors (like metal oxide semiconductor field-effect transistors-MOSFETs), in order to permit conduction, hole or electron dopants are used for the semiconductors. These electrons are affected by collisions with the impurities, resulting in undesirable effects in the transistor operation. HEMT transistors obviated this need, using a heterojunction of a highly doped wide-bandgap n-type donor-supply layer (AlGaAs) and a non-doped narrow-bandgap channel layer with no dopant impurities (GaAs). However, in the
AlGaN/GaN HEMT case, there is no need for doping for the channel creation, as in the AlGaAs case.

The operation principle of the HEMT transistor is based on the heterostructure properties. A heterostructure or heterojunction is formed between two semiconductors with different energy band-gaps $E_g$, permittivities $\varepsilon_s$, workfunctions $\varphi_s$, and electron affinities $\chi$. The energy band diagram of two semiconductors before getting in contact is shown in Fig. 2-2 (a). After the wide band gap semiconductor gets into contact with the narrow band gap semiconductor, a discontinuity in conduction band $\Delta E_c$ and valence band $\Delta E_v$ is present. When in contact, the energy bands of the two semiconductors bend because the energy Fermi ($E_F$) level must be continuous. Moreover, because of the discontinuity in the conduction band and the energy band bending, a triangular quantum well is formed, leading to the formation of the two-dimensional electron gas (2DEG) at the bottom side, as indicated in Fig. 2-2 (b).

![Fig. 2-2: Energy band diagram of two semiconductors (a) before getting in contact, (b) after getting in contact.](image)

The low energy 2DEG region has some nm of thickness, forming a thin channel, where the electrons pass through when traveling from source to drain. This is where the electrons gather, in order to minimize the total energy. Since the 2DEG is a very thin region, the electrons move only in two dimensions (2D), in order to keep their energy profile the lower possible [51]. Moreover, this way it is possible to separate the electrons in the channel from their donor atoms, reducing Coulomb scattering and thus increasing the mobility of the conducting electrons.

An AlGaN/GaN HEMT structure is illustrated in Fig. 2-3 (a). In thermal equilibrium (zero gate voltage), the band diagram of the structure underneath the gate electrode is shown in Fig. 2-3 (b). In Fig. 2-3 (c), the band diagram is shown after applying negative gate voltage. A Schottky barrier exists underneath the gate electrode, forming a quasi-insulating barrier between gate electrode and 2DEG. Depending on gate voltage, the triangular potential well formed at the AlGaN/GaN interface is raised or lowered in energy with the accumulation layer being emptied or filled (as shown in Fig. 2-3 (b) and (c) respectively). For very large gate bias, the depletion region penetrates into the 2DEG region, resulting in 2DEG concentration being negligible and current channel being pinched off. The corresponding gate voltage is called threshold voltage [52].
2.2 HEMT applications

As already mentioned, a HEMT is a transistor with a high electron mobility feature channel. Generally, the transistor can be used in switching applications (used in computer industry), for signal amplification and power conversion. In particular, HEMT transistors can be used in high-speed applications as well as in low noise, small signal amplifiers, power amplifiers, oscillators and mixers with high frequency operation. Therefore, HEMTs are used in radio frequency applications, including cellular telecommunications, radar, radio astronomy or anything requiring a combination of very high frequency and low noise [53].

More specifically, the application of HEMTs strongly depends on the materials used. For example, HEMTs using gallium arsenide (GaAs) are used in cellphones and radar systems, or HEMTs using gallium nitride (GaN) are used for high power applications (as mobile power transistors-3G, 4G transmitters, power transmission lines and radio frequency power transistors. This difference in application between GaAs and GaN based HEMTs, is due to the larger band gap of GaN, which permits high temperature and voltages operation [54].

AlGaN/GaN HEMTs are promising candidates for switching power transistors because of the high off-state breakdown strength combined with the excellent channel conductivity at on state. This important feature is due to the physical properties of GaN combined with its heterostructure material AlGaN.

For power devices there are many characteristics that matter in the variety of power conversion systems available today. Five of the most important are conduction efficiency, breakdown voltage, switching efficiency, size and cost. In the following Table (2-1) the GaN, Si and SiC materials electronic properties at 300 Kelvin are presented:
Chapter 2: High Electron Mobility Transistor

<table>
<thead>
<tr>
<th>Properties</th>
<th>GaN</th>
<th>Si</th>
<th>SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_G \text{ (eV)}$</td>
<td>3.4</td>
<td>1.12</td>
<td>3.2</td>
</tr>
<tr>
<td>$E_{BR} \text{ (MV/cm)}$</td>
<td>3.3</td>
<td>0.3</td>
<td>3.5</td>
</tr>
<tr>
<td>$V_S \text{ (-10^7 cm/s)}$</td>
<td>2.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$\mu \text{ (cm}^2\text{/V·s)}$</td>
<td>990-2000</td>
<td>1500</td>
<td>650</td>
</tr>
</tbody>
</table>

Table 2-1: GaN, Si and SiC electronic properties at 300 Kelvin [54].

A very important characteristic of the HEMT in high voltage applications is the breakdown voltage, the voltage at which the HEMT starts to degrade. Compared to Si, breakdown strength of GaN is more than 10 times higher. This practically means that 10 times the voltage applied to Si devices, can be applied to GaN for a given dimension. If the device is at the on state, the remaining on-state resistance defines the device losses. Moreover, the on-state resistance value scales with the device drift region length. In addition, due to electron transport properties of GaN/AlGaN HEMTs, the on-state resistance is almost two orders of magnitude lower, as compared to the Si situation, for the same voltage. To sum up, GaN devices can offer the advantage of high breakdown voltages and high current levels simultaneously as well as feature small semiconductor areas [55].

Based on the material properties, the theoretical minimum device on-resistance (the inverse of conductivity) is presented as a function of breakdown voltage, for GaN, Si and SiC materials (Fig. 2-4). As we can easily distinguish in this graph, the GaN and SiC materials exhibit superior behavior concerning the higher breakdown voltages combined with the lower on-resistance values. This fact results in smaller devices with electrical terminals closer together for a given breakdown voltage requirement. Moreover, GaN presents an extra advantage as compared to SiC, as a result of the enhanced mobility of electrons in the 2DEG. This translates into a GaN device with a smaller size for a given on-resistance and breakdown voltage [55].
2.3 2DEG electron mobility suppression factors

Regularly, in an AlGaN HEMT transistor, the 2DEG is formed at the junction between GaN and AlGaN, without defined borders of its start or ending, i.e. the 2DEG exists in between the two layers junction, taking place in both of them. AlGaN/GaN heterostructures have shown high mobility (~1500 cm²/V·s) and carrier sheet 2DEG concentration (~1x10²/cm²) values. The HEMT transistor performance is strongly affected by the carrier transport properties of the transistor channel. Moreover, the 2DEG properties in AlGaN/GaN heterostructures strongly depend on alloy composition and thickness of the AlGaN barrier layer [56].

2DEGs electron mobility is restricted by scattering mechanisms such as lattice (phonon) scattering, defect scattering (e.g. alloy disorder and dislocation scattering) and interface roughness scattering. At room temperature (RT), the mobility is dominated by polar optical phonon scattering, whereas interface and alloy disorder scattering dominate at lower temperatures.

Alloy disorder scattering is a reason for the carrier scattering in the AlGaN layer, due to the penetration of the 2DEG wavefunction into the barrier layer. More specifically, in the AlGaN wurtzite lattice, there are Al and Ga atoms randomly distributed such that the overall composition over any plane is constant over Al (Ga) planes. Thus, the carriers are scattered because of this atomic disorder (alloy scattering) [57]. This effect is especially pronounced while having a high 2DEG density (>7x10¹² cm⁻²) and a poor carrier confinement in the interface, resulting in the electron penetration into the AlGaN layer and to a further degradation of the 2DEG mobility [58].

A way to overcome this problem was proposed [59], by adding in between the heterojunction a thin enough AlN layer (limiting dislocation creation) and in this way,

![Fig. 2-5: The experimental data of 2DEG mobility (μ_exp) at 13K with its fitting curve (μ_fit) and the calculated component mobilities of the individual scattering processes as a function of Al content (x) in the AlGaN barrier layer [56].](image)

![Fig. 2-6: The experimental data of 2DEG mobility (μ_exp) at 13K with its fitting curve (μ_fit) and the calculated component mobilities of the individual scattering processes as a function of the AlGaN barrier layer thickness (d) [56].](image)
confining electrons to binary compounds (not alloys, thus not presenting alloy scattering) eliminates alloy scattering effects. This proposal was based on the fact that the carriers penetrate into AlN in a thickness of only 3Å [58].

Moreover, in a quasi 2DEG the charge transport takes place along the interface between two semiconductors. Thus, the interface roughness produces an additional deviation from the periodical lattice and so it is possible to result to a further reduction of the mobility of a 2DEG. Sharp heterointerfaces are therefore needed, in order to prevent the carrier scattering due to the interface roughness.

In Fig. 2-5, the experimental data of 2DEG mobility ($\mu_{\text{exp}}$) at 13K with its fitting curve ($\mu_{\text{fit}}$) and the calculated component mobilities of the individual scattering processes as a function of Al content (x) in the AlGaN barrier layer are presented. It is easily observed that the dominant scattering mechanisms are the alloy disorder scattering and the interface roughness scattering, with the latter overwhelming at higher values of x ($\geq 0.25$). The same situation is observed in the graph of Fig. 2-6, where the AlGaN layer barrier thickness is plotted versus mobility; again the dominant processes include alloy disorder and interface roughness scattering, with the latter overwhelming when $d>20$ nm. The effect of the other scattering mechanisms (especially the surface donor scattering mechanism) are stronger when $d$ is smaller than 10 nm [56].

### 2.4 2DEG formation mechanism

Many different 2DEG formation mechanisms have been proposed. However, most of them considered a priori the existence of 2DEG while trying to explain it. Moreover, the polarization fields cannot be responsible for the free electron creation, since they are related to the rearrangement of charges-bounds in the unit cell in order to form the 2DEG. But, these fields facilitate the electron transfer to the quantum well [60].

According to recent research [61], by splitting the heterostructure into two independent parts, analyzing separately and finally assembling together, we can have more clear physical pictures of the AlGaN/GaN heterostructure and the process of the 2DEG formation. As already mentioned, the polarization effect of an AlGaN layer grown on a GaN buffer induces positive polarization charges at the AlGaN/GaN interface and negative polarization charges at the top of the AlGaN layer. Thus an electric field is formed within the AlGaN layer. If we consider an undoped AlGaN layer, due to the fact that no conductive electrons exist, under the electric field, the energy band will almost remain unaffected. Moreover, no or few electrons will flow to the GaN layer (having the Fermi levels close to each other), after being in contact, making the formation of 2DEG impossible.

The formation of the 2DEG at the AlGaN/GaN interface can be easily explained by assuming the existence of donor states on the AlGaN surface [62], [63]. In Fig. 2-7, the energy band of a freestanding AlGaN layer with surface donor states is shown, supposing that the AlGaN layer is under the same tensile strain as grown on GaN. When the AlGaN layer is very thin, the surface donor levels lie below the conduction-band minimum (CBM) of GaN,
and no electrons are supplied to the potential well at the AlGaN/GaN interface [64]. Once the AlGaN layer is thick enough, the Fermi level will approach the donor state level $E_d$, and the electrons will be driven into the conductive band and pushed towards the other side by the force of the polarization-induced electric field. When GaN gets in contact with the AlGaN layer, due to the lower Fermi level, the electrons will easily flow into the GaN layer, accumulating at the interface and forming the 2DEG as shown in Fig. 2-8.

Fig. 2-7: Energy band of undoped AlGaN, assuming that surface donor states exist. Electrons are driven into the conductive band and move under the force of the polarization-induced electric field.

Fig. 2-8: Energy band of an undoped AlGaN/GaN heterostructure. When contacting a GaN layer, electrons will flow into the GaN side, accumulate at the interface and thus form 2DEG.

Moreover, according to J. P. Ibbetson et al. [65], the source of free electrons for the 2DEG formation derives from the ionized donors in the AlGaN barrier and the ionized donor-like surface states. The following equation explains the charge neutrality in the absence of an external electric field:

$$\sigma_{\text{surface}} + \sigma_{\text{AlGaN}} + \sigma_p + (-\sigma_p) + (-q \cdot n_s) = 0$$

(2-1)

where $\sigma_{\text{surface}}$ is the charge due to the ionized donors; $\sigma_{\text{AlGaN}}$ is the integrated sheet charge due to ionized donors; $\sigma_p$, $-\sigma_p$ are the fixed polarization-induced charges at the AlGaN/GaN interface and surface respectively; $-q \cdot n_s$ is the negative sheet charge due to the electrons in 2DEG.
The above equation (2-1) is transformed as follows:

\[ q \cdot n_s = \sigma_{\text{surface}} + \sigma_{\text{AlGaN}} \]  

(2-2)

However, for a truly undoped AlGaN barrier, \( \sigma_{\text{AlGaN}} = 0 \), so any 2DEG electrons are due to donorlike surface states.

In the following Fig. 2-9, we consider an undoped AlGaN barrier layer, having a surface state at energy \( E_D \). The difference between \( E_F \) and \( E_D \) decreases with increasing thickness of AlGaN, as illustrated in Fig. 2-9. When reaching a critical AlGaN thickness, the donor state energy comes equal to the Fermi level energy. As a consequent, the electrons can now travel from the occupied surface states to empty conduction band states at the interface, forming the 2DEG. Fig. 2-10 shows the 2DEG density dependence on the AlGaN thickness, with Al doping 34%, according to [65], after the appropriate theoretical calculations. The Hall results (dots) were consistent with the single surface donor model (solid line). No 2DEG formation was observed for an AlGaN barrier thickness of almost 35Å.

![Fig. 2-9: Band diagram showing the surface donor model with the AlGaN thickness (a) below critical thickness for 2DEG formation and (b) beyond critical thickness for 2DEG formation.](image)

![Fig. 2-10: Room temperature 2DEG density versus Al\(_{0.34}\)Ga\(_{0.66}\)N thickness.](image)

In the following figures the results of the study of L. Hsu and W. Walukiewicz [60] are presented. In Fig. 2-11 (a), the 2DEG density dependence as a function of the Al content is presented, with a thickness of 31 nm and an Al content of 27%. It is clearly observed that an almost linear relationship exists. The dependence of the 2DEG density when compared with the AlGaN thickness is presented in Fig. 2-11 (b), with Al composition 27%. In both cases, the solid line is based on theoretical calculations and is in very good agreement with the experimental results.
According to Fig. 2-12, for very thin AlGaN barrier layers (<30Å for a layer with 25% Al composition and <160Å for a layer with 5% Al composition) the already mentioned \( E_D \) donor state energy is below the Fermi level energy and so the surface charges are neutral. In this case, the only electrons that can travel and form the 2DEG are the unintentional dopants in the bulk AlGaN. For thicker barrier thicknesses (and of course \( E_D > E_F \)), the electrons are transferred and the 2DEG density increases rapidly [60].

Fig. 2-11: (a) 2DEG density as a function of Al composition in an AlGaN barrier of 31nm thickness, (b) 2DEG density as a function of the barrier thickness for an AlGaN barrier with 27% Al. The experimental points are taken from [62].

Fig. 2-12: 2DEG density as a function of AlGaN barrier width for three different Al composition barriers [60].

2.5 AlGaN/AlN/GaN structure properties

According to Shen et al. [66], if a 1nm thick AlN layer is inserted in between the AlGaN/GaN heterojunction, the electrical properties of the structure are clearly enhanced, e.g. the room-temperature Hall mobility was measured 1540 cm²/V·s and the 2DEG density 1.48x10¹³/cm². This can be explained by the discontinuity between the AlGaN and GaN
layers resulting to an increased $\Delta E_c$, reducing the penetration of carriers from the GaN channel into the AlGaN layer and the effect of the alloy disorder scattering in AlGaN.

Thus, when inserting the AlN layer (6.2 eV bandgap) in between the heterojunction, it serves as a barrier layer, not permitting the electrons insertion in the AlGaN layer (and consequently suppressing the alloy disorder effects), forcing all the electrons towards the GaN layer. The large AlN energy bandgap increases the difficulty of carriers escaping the quantum well. Moreover, the peak electron density is increased because of the bigger difference in spontaneous polarization of AlN and GaN compared with that of AlGaN and GaN. Due to the fact that AlN is a binary material, it doesn’t exhibit alloy disorder effects.

It is worth mentioning that the sharpness of the AlN/GaN interface strongly affects the disorder scattering effects suppression [67].

Fig. 2-13 (a) and (b) show characteristic plots of Hall mobilities ($\mu_{\text{Hall}}$) and sheet resistances ($\rho_s$) measured at room temperature (RT) and 77 K, respectively, with respect to the AlN layer thickness. It is clearly observed that Hall mobility and sheet resistance vary with the AlN layer thickness. The optimum Hall mobility combining a low sheet resistance was found for 1nm AlN thickness, showing 1770 $\text{cm}^2/\text{V} \cdot \text{s}$ with 365 $\Omega/\text{sq}$ at RT and 7260 $\text{cm}^2/\text{V} \cdot \text{s}$ with 87 $\Omega/\text{sq}$ at 77 K ($2\text{DEG density} \, n_s = 1.0 \times 10^{13}/\text{cm}^2$) [68].

![Fig. 2-13: A characteristic plot showing the Hall mobility ($\text{cm}^2/\text{V} \cdot \text{s}$) and the sheet resistance ($\Omega/\text{sq}$) with respect to the thickness of the AlN layer (nm) (a) at room temperature (RT) and (b) at 77K.](image)

However, after exceeding a critical thickness of about 1nm, the 2DEG’s mobility is deteriorating, probably because of an increase in the dipole scattering due to strong polarization fields [67].
Chapter 3: Advanced Microscopy Techniques

3.1 STEM-HAADF method

Scanning Transmission Electron Microscopy (STEM) is an excellent tool for the nanostructures characterization. It can be used for the elemental composition and crystal information at atomic scale. The process used by the STEM technique is based on the same principle as a normal scanning electron microscope (SEM): it uses a focused electron beam passing into a very small spot which is scanned over the sample. The basic difference of STEM with SEM procedure is that in STEM the preparation of ultrathin specimens of 200 nm or less (except for nanoparticles) is needed so that the accelerated beam of electrons passes through the sample. Finally, this electron beam interacts with the TEM sample and a detector collects the transmitted beam. This detector can either be a CCD chip (when operating in TEM mode) or a High Angle Annular Dark Field (HAADF) detector (when operating in STEM mode).

![Fig. 3-1](image)

When operating in STEM mode, the electron beam is focused into a small point on the specimen. As the beam is rastered across the specimen, the forward scattered electrons at each raster point are counted and the resulting electron counts and x/y locations on the specimen are turned into an image. More specifically, the principle of scanning-image formation is shown in Fig. 3-1. By adjusting the scan coils, the beam is scanned on the specimen. The same coils are used for the scanning of the computer display simultaneously. The electron detector acts as the interface between electrons deriving from the specimen and the image viewed on the display screen. However, the process of creating a STEM image is much slower than a TEM image. In this way, a variable, direct-beam signal goes from the detector to modulate the signal on the computer display, forming a Bright Field (BF) image [69].

As already mentioned, when working in STEM mode, the direct or scattered beams are selected, by not using apertures as in TEM mode, but detectors. The characteristic of STEM
that does not use lenses for the image formation, results in the fact that defects of lenses do not affect the image resolution (e.g. chromatic aberration is absent in STEM images). The operational modes of TEM (Dark Field and Bright Field) and STEM (Dark Field and Bright Field) are shown schematically in Fig. 3-2. Thus, a BF-on-axis detector or an annular DF (ADF) detector are placed in a plane that is conjugate with the back focal plane. We control which electrons fall on which detector and thus contribute to the image by adjusting the post-specimen (imaging) lenses to change the camera length. For DF imaging, the ADF detector clearly gathers more electrons as compared to the objective aperture [69].

![Fig. 3-2: Comparison of the use of an objective aperture in TEM to select (A) the direct or (B) the scattered electrons forming BF and DF images, respectively. In STEM we use (C) an on-axis detector or (D) an off-axis annular detector to perform equivalent operations.](image)

More specifically, similarly to TEM imaging, for the bright field imaging, a bright field detector (working just like a TEM aperture) is placed in the axis of the microscopy, intercepting the direct-beam electrons no matter where the beam is scanning on the specimen. The Dark Field (DF) images in STEM mode are formed by selecting any or all of the scattered electrons. Usually, an annular detector is used for this purpose that surrounds the BF detector, making all scattered electrons fall onto that detector. This process is called annular dark-field imaging (ADF). The ADF detector is centered on the optic axis and has a hole in the middle, within which the BF detector sits. Another way that an annular detector can be used, is by being sited around the ADF and picking electrons scattered out to even higher angles, called high-angle ADF (or Z-Contrast).

In a STEM DF image, the scattered electrons fall onto the ADF detector. However, there is a fundamental difference between the TEM and STEM DF modes: DF TEM images are
usually formed by permitting only a fraction of the scattered electrons to enter the objective aperture and STEM images are formed by collecting most of the scattered electrons on the ADF detector [69].

### 3.1.1 Annular dark field imaging

Annular dark-field imaging is a method used for the mapping of samples in a scanning transmission electron microscope (STEM). Collecting scattered electrons with an annular dark-field detector forms these kinds of images. In traditional dark-field imaging (in a parallel beam mode, not STEM), an objective aperture is placed in the diffraction plane so as to only collect electrons scattering through that aperture, avoiding the main beam. By contrast, in STEM mode the optics distinguishing between dark and bright field modes is positioned further downstream, after the converged beam has interacted with the specimen. Consequently, the contrast mechanisms are different between conventional dark field imaging and STEM dark field [69].

There are generally two types of DF-STEM detectors, which differ only in the scattering angles that are sampled. A dark field detector that collects electrons scattered at slightly higher angles than those found in BF-STEM images is generally simply called a dark field STEM detector (and the images it forms are referred to as DF-STEM). DF-STEM images can also include electrons involved in things like diffraction contrast. A detector that only collects very highly scattered electrons is generally called a high angle annular dark field STEM detector (and the images it forms are referred to as HAADF-STEM images).

An annular dark field detector collects electrons from an annulus around the beam, sampling far more scattered electrons than can pass through an objective aperture. An annular dark field image formed only by very high angle, incoherently scattered electrons — as opposed to Bragg scattered electrons — is highly sensitive to variations in the atomic number of atoms in the sample (Z-contrast images). This technique is also known as high-angle annular dark-field imaging (HAADF) [70]. A schematic of the HAADF detector setup for Z-contrast imaging in a STEM is shown in Fig. 3-3. Z-contrast is called a high-resolution (atomic) mass thickness (Z) imaging technique. Bragg effects are avoided if the HAADF detector only gathers electrons scattered through an angle greater than 50 mrad. The conventional ADF and BF detectors are also shown along with the range of electron scattering angles gathered by each detector [69].
3.1.2 Signals in STEM mode

Generally, there is a wide range of possible signals available in STEM mode, detected and plotted as a function of probe position (for the formation of a magnified image). The most common of them are presented below [71]:

1. Transmitted electrons exiting the sample at low angles with respect to the optic axis (BF mode).
2. Transmitted electrons exiting the sample at high angles with respect to the optic axis (ADF mode).
3. Transmitted electrons having lost an amount of energy after passing through the sample (electron energy loss spectroscopy EELS).
4. X-rays generated from electron excitations in the sample (EDX).
As already mentioned, due to its excellent properties, SiC is the ideal material for high power applications. Among others, metal oxide semiconductor field effect transistors (MOSFETs) grown on 4H-SiC are considered to be a very nice alternative for silicon insulator gate bipolar transistors (IGBTs) replacement. Indeed, MOSFETs grown on 4H-SiC can result in lower static and dynamic losses, with higher switching frequencies operation than IGBTs, and also can provide a higher efficiency in power converters [72].

However, a problem searching for solutions exists in SiC/SiO₂ structures: There is a large concentration of interface-states at the interface, trapping free carriers and acting as Coulomb scattering sites, therefore reducing the channel mobility. One of the solutions proposed concerns use of post-deposition-annealing (PDA) processes in dinitrogen oxide N₂O or phosphoryl chloride POCl₃. Recent research studies showed that N or P atoms not only act as passivating species for SiO₂/SiC interface traps but they are also incorporated in a region of few nm in 4H-SiC (below interface) presenting densities in the order of 10¹⁴ cm⁻² [73].

Currently, power devices (e.g. MOSFET etc.) are grown on SiC with an intentional misorientation angle from the (0001) plane in order to exploit the fact that the misoriented growth results to a better step-control and polytype stabilization. According to T. Kimoto et al. [74], using step-controlled epitaxy, the polytype of the epilayers can be easily controlled by surface steps existing in the off-oriented substrates. Moreover, for materials economy reasons, a lower off cut is essential. In order to manage the growth of a good crystal quality of 2 deg cut off material, the optimization of growth parameters is widely studied. However, the difficulty to control the surface roughness, surface defects and polytype inclusions at low misorientation angles is still a problem searching for solutions [75].

The MOS capacitor structure, grown by NOVASIC and processed at CNR, consists of an n-type epitaxial layer (with a donor concentration of about 5×10¹⁵ cm⁻³) grown on a heavily doped 4H-SiC substrate, with a misorientation angle of 2°-off axis. After growth, a chemical mechanical planarization (CMP) process was carried on the sample surface. Then, a SiO₂ layer of around 50 nm-thickness was deposited as gate dielectric and was subjected to a standard N₂O or POCl₃ post deposition annealing (PDA) process. Poly-Si and Ni-based Ohmic contact were used as gate electrode and sample backside contact, respectively. A schematic view of the fabricated MOS capacitor is shown in Fig. 4-1. The SiO₂/SiC interface is characterized under a structural (using CTEM and HRTEM) and electrical point of view. The results of the structural analysis prior and after the CMP process for both N₂O and POCl₃ post deposition annealing processes are presented and discussed in the following paragraphs [37]. Some interesting electrical results are also referred.
4.1 \textbf{N}_2\text{O} \text{ post-deposition annealing}

\textbf{4.1.1 Before CMP treatment}

The following TEM results concern the as-grown structure: the 4H-SiC epilayer on the 2 deg off axis 4H-SiC (Si-faced) using \text{N}_2\text{O} post deposition annealing process, before CMP process. The electron diffraction pattern (Fig. 4-2), taken along $[1\bar{1}0]$ SiC, confirms the presence of 4H-SiC.

In Fig. 4-3, the step bunching on the 4H-SiC is observed in a low magnification TEM image. The white arrows show the step bunching positions. An amorphous SiO$_2$ layer is shown on the 4H-SiC epilayer, with a thickness of about 55 nm. It can be clearly observed that the oxide layer treated in N$_2$O exhibits in its surface a conformal coating, i.e., it shows
periodical undulations (steps) along the [1100] direction, following the step bunching of the 4H-SiC substrate grown on.

![Fig. 4-3: A TEM image showing the ascending steps of the 4H-SiC surface.](image)

In Fig. 4-4, in higher resolution, the TEM image reveals better the characteristics of the ascending bunching steps. According to Hiroyuki Matsunami et al. [75], the number of Si-C bilayers of the step height in the 4H-SiC case is mostly two (2) or four (4), with four (4) being the most dominant. Indeed, in our case, the bunched steps dominant height is four (4) Si-C bilayers, corresponding to the unit cell of 4H-SiC (AaBbCcBb). Such a bunched step is shown in the magnified part of Fig. 4-4, presented as inset. In addition, no epitaxial-induced defects are observed, like pits and triangular defects, which could degrade devices’ performance.

![Fig. 4-4: A HRTEM showing the step bunching in the 4H-SiC/SiO2 interface.](image)

Before the oxide growth, the surface morphology of the 4H-SiC epilayer was inspected by Atomic Force Microscopy (AFM), shown in Fig. 4-5. The root mean square (RMS) value of the height distribution is 8.67 nm (before CMP treatment) [76].
4.1.2 After CMP treatment

The following TEM results concern the characterization of the structure consisting of the 4H-SiC epilayer on the 2 deg off axis 4H-SiC (Si-faced) using N$_2$O post deposition annealing process, after CMP process. Moreover, a poly-silicon layer was grown on top of the described structure. A typical electron diffraction pattern, shown in Fig. 4-6, taken from a selected area containing part of the substrate and the amorphous layer (along [11\(\bar{2}\)0] SiC) confirms the presence of 4H-SiC.

In Fig. 4-7, a combination of conventional bright field TEM images from a cross-sectional specimen shows the structure of the film. An amorphous SiO$_2$ layer is observed on top of the 4H-SiC layer, with a thickness of about 47-49 nm. Above the SiO$_2$ layer, a poly-Si layer, with a thickness of about 220-235 nm is seen. The presence of glue in the upper part of the image indicates the end of the film. No step-bunching is observed at the 4H-SiC/SiO$_2$ interface at this magnification. However, in larger magnifications, the high resolution TEM study reveals
the presence of some steps, of about 1-2 atomic planes height, presenting an almost smooth oxide/semiconductor interface (Fig. 4-8).

![Fig. 4-7: A TEM image showing no step bunching in the 4H-SiC/SiO₂ interface after CMP process.](image)

![Fig. 4-8: A HRTEM image showing the presence of steps (1-2 Si-C bilayers height) at the 4H-SiC/SiO₂ interface after CMP process.](image)

The same results are verified from the AFM measurements. As illustrated in Fig. 4-9, the semiconductor surface subjected to a CMP process appears flat, with a root-mean-square (RMS) roughness of 0.14 nm for a scanned area of 10×10 μm². This value is significantly lower than that measured before CMP, of around 9 nm [37]. Thus, the surface roughness is reduced by more than one order of magnitude.

![Fig. 4-9: AFM scan of the 4H-SiC semiconductor surface before the oxide deposition and after CMP treatment [37].](image)
4.2 POCl₃ post-deposition annealing

4.2.1 Before CMP treatment

The following TEM results concern the as-grown structure: the 4H-SiC epilayer on the 2 deg off axis 4H-SiC (Si-faced) using POCl₃ post deposition annealing process, before CMP treatment. The electron diffraction pattern (Fig. 4-10), taken along [11\overline{2}0] SiC, confirms the presence of 4H-SiC.

![Fig. 4-10: A typical electron diffraction pattern taken along [11\overline{2}0] 4H-SiC substrate.]

In Fig. 4-11, the step bunching of the SiC substrate is observed. An amorphous SiO₂ layer is shown on the SiC substrate, with a thickness of about 55-60 nm. In this case, before CMP treatment, the oxide layer treated in POCl₃ exhibits in its surface fewer undulations (steps) along the [\overline{1}100] direction, exhibiting a high degree of planarization in respect to the N₂O treatment situation.

![Fig. 4-11: A TEM image showing the descending steps indicated with white colored arrows.]

Moreover, recent research [77] concerning 4 deg. off axis 4H-SiC MOS structure showed a significant diffusion of Phosphorus in the oxide insulating layer, homogeneously distributed in it, during POCl₃ annealing. During annealing, this amount of Phosphorus results in the formation of a phosphosilicate glass and thus in the smoothening of the SiO₂ surface observed in Fig. 4-11. Furthermore, it is well known that P-doped SiO₂ can soften and reflow above
950 °C, creating a smooth topography that is beneficial for the subsequent poly-Si deposition [77].

The following HRTEM image (Fig. 4-12) shows in higher resolution the step-bunching situation that exists, revealing mostly the presence of two and four Si-C bilayers height steps. More specifically, a characteristic step is magnified in Fig. 4-12, presenting four (4) Si-C bilayers height, corresponding to the unit cell of 4H-SiC (AaBbCcBb).

In addition, no epitaxial-induced defects are present in this case too, like pits and triangular defects, which could degrade devices’ performance.

![HRTEM image showing the step-bunching in the 4H-SiC/SiO₂ interface.](4H-SiC-SiO₂.png)

**Fig. 4-12:** A HRTEM image showing the step-bunching in the 4H-SiC/SiO₂ interface.

### 4.2.2 After CMP treatment

The following TEM results concern the characterization of the structure after CMP treatment, using POCl₃ post deposition annealing process: it consists of the 4H-SiC epilayer on the 2 deg off axis 4H-SiC (Si-faced) with poly-silicon grown on top. A typical electron diffraction pattern, shown in Fig. 4-13, taken from a selected area containing part of the substrate and the amorphous layer (along [1120] SiC) confirms the presence of 4H-SiC.

![Typical electron diffraction pattern](1120.png)

**Fig. 4-13:** A typical electron diffraction pattern taken along [1120] 4H-SiC.
In Fig. 4-14, a conventional TEM image shows the accurate structure of the sample. As in the previous sample, an amorphous SiO₂ layer is shown on the 4H-SiC substrate, with a thickness of about 52-65nm. The SiO₂/poly-Si interface is not sharp, resulting to a non-uniform SiO₂ thickness along the sample. Above the SiO₂ layer there is a poly-Si layer, with a thickness of about 265-308nm. The presence of glue in the upper part of the image indicates the end of the film.

**Fig. 4-14:** A TEM image showing the structure of the sample.

Fig. 4-15 is a combination of TEM images exhibiting a stepped 4H-SiC/SiO₂ interface. The steps’ positions are indicated by black colored arrows. A TEM image in higher magnification is seen in Fig. 4-16 where two steps are indicated by white colored arrows.

**Fig. 4-15:** A TEM image showing steps in the 4H-SiC/SiO₂ interface.
In Fig. 4-17, a high resolution TEM image shows an individual step in the 4H-SiC/SiO\(_2\) interface. The steps' height is about 9 atomic planes (more than two unit cells of 4H-SiC).

However, in other sites of the sample, steps of 1-2 atomic planes are observed, as shown in the next HRTEM image (Fig. 4-18). It is clearly observed that in this case, after CMP process, the 4H-SiC surface is smooth, but some few regions with more than four Si-C bilayers step height still exist.
4.3 Specimen comparison

In both cases (after N₂O/POCl₃ post deposition annealing), before CMP treatment, the 4H-SiC surface presents a step-bunching situation (parallel to [1\tilde{1}00]), where the most dominant step height is four (4) bilayers of Si-C, which corresponds to the unit cell of 4H-SiC. However, two bilayers height steps are also observed in both cases. In addition, no epitaxial-induced defects are observed, like pits and triangular defects, which could degrade devices’ performance. The SiO₂ thickness was measured around 48-57nm, very close to the nominal value, as expected according to the deposition conditions. However, the oxide layer treated in POCl₃ exhibits in its surface fewer undulations (steps) along the [1\tilde{1}00] direction, exhibiting a higher degree of planarization in respect to the N₂O treatment situation. This situation is clearly illustrated in Fig. 4-19, where the structure after N₂O PDA and after POCl₃ PDA is shown in (a) and (b) respectively.

Moreover, recent research [78] concerning 4 deg off axis 4H-SiC MOS structure, showed a significant diffusion of Phosphorus in the oxide insulating layer, homogeneously distributed in it, during POCl₃ annealing. During annealing, this amount of Phosphorus results in the formation of a phosphosilicate glass and can explain the planarization degree of the SiO₂ surface observed in Fig. 4-19 (b) (which differs from the undulated SiO₂ surface after N₂O PDA annealing). Furthermore, it is well known that P-doped SiO₂ can soften and reflow above 950 °C, creating a smooth topography that is beneficial for the subsequent poly-Si deposition [77]. Thus, a different surface morphology of the oxide treated in POCl₃ is observed, as a consequence of the strong incorporation of Phosphorus in the oxide layer during annealing procedure, passivating the interface states and so enhancing the channel mobility [79].

Finally, the CMP process results in a good quality SiO₂/SiC interface, where the 4H-SiC interface becomes smooth enough (presenting 1-2 atomic layers height), with only some few cases of greater steps height.

![Fig. 4-19: TEM images showing the structure (a) after N₂O post-deposition annealing (PDA) and (b) after POCl₃ post-deposition annealing (PDA).](image-url)
4.4 Electrical characteristics of SiO₂/4H-SiC (2 deg off-axis) interface-Effect of CMP process

In Fig. 4-20, the interface state density profile as a function of energy from the conduction band edge (Eₖ) is presented. The C-V and G/ω-V measurements results, acquired at 10kHz and at room temperature respectively, are presented as inset. Small Dᵢᵣ values near the conduction band edge is a very important parameter for MOS structures, due to the fact that SiC MOS transistor performance is mainly limited by the interface states at shallow energies [80].

Indeed, as shown in Fig. 4-20, a Dᵢᵣ value of 1×10¹² eV⁻¹cm⁻² below the conduction band is observed. The Dᵢᵣ profile decreases from the conduction band edge towards the mid-gap. These characteristics are comparable with those reported for the standard 4 deg off axis material in the same energy range (0.2-0.4 eV) [81]. Moreover, the reliability of the oxide was proofed through time-zero-dielectric-breakdown (TZDB) measurements. Thus, PDA treatment in ambient N₂O exhibits a beneficial effect on the SiO₂ insulator and SiO₂/4H-SiC interface properties due to the passivation of oxide defects and interface traps [82].

Concerning the electrical behavior before and after CMP process, the electrical characterization showed that the value of the oxide electric breakdown field was 7.4 MV/cm before CMP. On the other hand, the breakdown value was increased to 9.5 MV/cm (as an average from measurements on several MOS capacitors) with the CMP technique, denoting its beneficial role [37]. Moreover, these results as well as the computed interface state density in the low 1×10¹²eV⁻¹cm⁻² range are comparable with the results that have been typically measured in the case of 4 deg off-axis 4H-SiC substrates, paving the way to the 2 deg off oriented SiC substrates device fabrication [37].

![Fig. 4-20: Dᵢᵣ distribution determined by admittance spectroscopy. In the inset, representative C-V and G/ω-V curves of the 2 deg-off-axis 4H-SiC MOS capacitors [37].](image-url)
Chapter 5: Experimental Results

Heterostructures grown on Si (111) substrates

5.1 Si heteroepitaxy characteristics and issues

The aluminum gallium nitride (AlGaN)/gallium nitride (GaN) compound semiconductor material system exhibits many interesting properties making it an ideal candidate for both electronic and optoelectronic devices. In addition to its large band gap (GaN 3.4 eV, aluminum nitride (AlN) 6.2 eV), high breakdown electric strength (1–3\times10^{10} \text{ V/cm}), high electron saturated drift velocity (2.2\times10^{10} \text{ cm/s}) and good thermal stability, the AlGaN/GaN heterojunction exhibits large conduction band discontinuity and strong spontaneous and piezoelectric polarization effect. This fact results in high concentration of 2-dimensional electron gas (2DEG) near the interface, allowing incorporation of a large electric field (>10^6 \text{ V/cm}) and high sheet charge (>10^{13} \text{ cm}^{-2}) without any doping. So, the AlGaN/GaN high electron mobility transistor (HEMT) has a larger potential application in the high-frequency, high-temperature and large-power areas [83], [84].

The heteroepitaxy of GaN on sapphire and silicon carbide (SiC) has been proven to be a great success, partly because native substrates of GaN are still very expensive. Besides sapphire and SiC, silicon (Si) is an attractive alternative substrate, offering several advantages such as high thermal conductivity (130 \text{ W/(m·K)}), the availability of low-cost large wafers (12-inch wafer available), and the opportunity of integration with other Si electronics. However, because of the high substrate temperatures (>1000 \text{ °C}) required during metalorganic chemical vapor deposition (MOCVD) growth, a large tensile stress can occur during cooling, causing cracks in the GaN epitaxial layers, because of the large mismatch in the thermal expansion coefficients of GaN (5.59 \times 10^{-6} \text{ K}^{-1}) and Si (3.59 \times 10^{-6} \text{ K}^{-1}). Moreover, this mismatch results in bowing of the Si wafers, which makes the lithography process difficult during device fabrication [85]. Furthermore, the large lattice mismatch between GaN and Si (~17%) leads to the formation of high-density dislocations during the initial growth and cooling process. Another problem is referred as chemical reactivity between Ga and Si, leading to melt back etching at elevated temperatures during metalorganic vapor phase epitaxy (MOVPE) of GaN. Direct outcomes besides cracking of epitaxial layers are the presence of high dislocation density of grown material and roughening of the layers surface [86], [87].

The management of stress and the achievement of crack-free GaN based heterostructures is a very important issue for the growth of good-quality GaN on silicon and promising results have been reported. More specifically, it was reported [88] that a low temperature (LT)-AlN interlayer could be used to relieve the tension stress in the GaN films grown on the Si substrate and then reduce the cracks in the grown GaN epilayer. Moreover, it could also prevent the threading dislocations from propagating into the overlying GaN. Other ways reported in order to avoid cracks in the GaN layer make use of patterned Si substrates.
(offering free facets to release the large tensile stress from thermal mismatch) or compositionally graded AlGaN layers [86], [87].

However, the use of LT-AlN interlayers is a time-consuming complex method due to the frequent ramping of temperature, V/III ratio and pressure during growth, giving rise to non-uniformity. Moreover, the growth on patterned silicon substrates is not convenient because it requires extra processing before growth. Finally, graded AlGaN intermediate layers have been successfully introduced in between the GaN layers, in order to prevent cracking of the GaN [89], [90].

In the following paragraphs, we report on the structural characterization of AlGaN/GaN heterostructures grown on Si (111) substrates by MOVPE. Two types of substrates were used: on axis and 4 deg cut off. The growth conditions of samples and the structural characterization results are analyzed and explained in detail.

5.2 Experimental

5.2.1 Sample Preparation

The epitaxial growth of the heterostructures on Si (111) substrate was carried out using EMCORE Turbodisc™ D75 MOCVD system operating at low pressures. Trimethylgallium (TMG), trimethylaluminum (TMA), and ammonia (NH3) were used as Ga, Al and N precursors, respectively. The substrates were cleaned using solvents, and then subjected to an in situ thermal cleaning in flowing H2 at 1100°C for 10 min.

A nucleation AlN layer was deposited with a few seconds TMA preflow before ammonia was introduced into the reactor, in order to prevent thick SiN formation and preserve in the nitride part the epitaxial orientation of trigonal Si (111) symmetry. Moreover, a high temperature AlN layer (HT-AlN) layer was deposited at low V/III ratio, at 1230°C temperature and 30Torr pressure, in order to provide a smooth AlN surface and some selection of exact c-plane orientated nucleation grains after full layer growth. According to XRD measurements, the AlN layer growth conditions used resulted in almost normal c-plane orientation to the substrate surface regardless of Si (111) tilt (in both substrate types: on axis and 4-deg off to (111) plane). The rest of the multi-AlGaN buffer structure was deposited in standard MOVPE growth conditions with strain/bow engineering described below.

Two sets of samples consisting of a buffer multilayer structure (#TG1934 and #TG1935) and one of a HEMT structure (#TG1931) were grown on Si (111) substrates using standard strain engineering approach of multi-AlGaN intermediate layers. The buffer multilayer structures, consist of nine different layers grown on “on-axis” and 4 deg off Si (111) substrate respectively. In the HEMT structure, after the deposition of the multilayer buffer structure (grown on “on-axis” Si substrate), the AlGaN/AlN/GaN heterostructure was deposited, as well as a final GaN layer as a cap layer. The layers of the epi-structures are illustrated in Fig.

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5-1 and 5-2 for the buffer and HEMT structures respectively and their nominal thicknesses described in Table 5-1.

![Fig. 5-1: The proposed buffer multilayer structure to be grown on Si (111) substrate.](image1)

![Fig. 5-2: The proposed HEMT multilayer structure to be grown on Si (111) substrate.](image2)

<table>
<thead>
<tr>
<th>Layers numbering</th>
<th>Layers (bottom to top)</th>
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<th>Nominal thickness (nm) for HEMT sample</th>
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<td>25</td>
</tr>
<tr>
<td>2</td>
<td>AlN-HT</td>
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<tr>
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<td>GaN</td>
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<td>100</td>
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<td>10</td>
<td>GaN undoped channel</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>AlN spacer layer</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>AlGaN (~20%)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>GaN cap</td>
<td>2-2.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-1: Nominal thicknesses of the buffer samples (#TG1934, #TG1935) and the HEMT sample (#TG1931) examined.
5.3 TEM Analysis: Results and discussion

The MOVPE-grown wafers were characterized by conventional (CTEM) and high-resolution (HRTEM) transmission electron microscopy (TEM). Cross-sectional TEM analysis was performed with a JEOL 2010 system operated at 200 keV, in order to study the structure of the layers, the quality of interfaces and the presence of defects in the layers. TEM specimens were prepared using traditional methods, as for example described in [91].

5.3.1 Multilayer Buffer Sample #TG1934-on axis

Cross-sectional TEM analysis took place for the structural characterization of epilayers and interfaces. The conventional bright field image of Fig. 5-3 shows the multilayer structure of the specimen grown on the on axis Si (111) substrate. In the upper part of the structure, the glue indicates the end of the sample. The elemental composition written on the layers is the nominal one, given by the growers (according to the preparation conditions). Table 5-2 gives the nominal and experimental thicknesses of the layers (from bottom to top) for buffer sample #TG1934:

<table>
<thead>
<tr>
<th>SAMPLE #TG1934 – on Si (111): p resistive 675 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layers numbering</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
</tbody>
</table>

Table 5-2: Nominal and experimental layers thickness for buffer sample #TG1934.

* It refers to the overall thickness of AlN-1 and HT-AlN layers.
Chapter 5: Experimental Results

Fig. 5-3: A low magnification TEM image showing the buffer multilayer structure grown on Si (111) substrate for buffer sample #TG1934 [92].

The electron diffraction study reveals that the layers were grown epitaxially on the Si substrate, besides the lattice mismatch on the interface plane. An example is shown in Fig. 5-4, obtained from a selected area containing part of the Si substrate and the first grown layers (along [110] Si). The epitaxial relationships are: the [111] Si direction is parallel to the [0001] AlN direction, the [11\bar{2}] Si direction is parallel to [1\bar{1}00] AlN direction and the [\bar{1}10] Si direction is parallel to [1120] AlN direction.

The main spots of the two phases are indicated with open and dashed circles for Si and AlN respectively.
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In Fig. 5-4, the corresponding electron diffraction pattern (obtained from a selected area containing part of the upper GaN layer and the intermediate AlGaN layers) shows the very good epitaxial growth of GaN on the AlGaN layers. The main spots of the two phases are indicated with arrows. Similar to this are also the patterns at the other interfaces.

In the following paragraphs we discuss the obtained results starting from bottom to top.

**Fig. 5-4:** A typical electron diffraction pattern obtained from a selected area containing Si substrate and the first AlN layers along $[\bar{1}10]$ Si. The very good epitaxial growth of AlN layers on the Si (111) substrate is revealed [92].

**Fig. 5-5:** An electron diffraction pattern obtained from a selected area containing GaN and AlGaN layers along $[\bar{1}10]$ Si. The very good epitaxial growth of GaN layers on the AlGaN intermediate layers is revealed.
(i) The Si substrate/AlN-1 interface

It should be noted that in the on-axis situation, a thin amorphous interlayer probably SiNₓ, was revealed by HRTEM at the AlN-1/Si substrate interface (Fig. 5-6), as also mentioned in the work of Kaiser et al. [93]. The layers thickness is not homogeneous in all areas, varying from around 0.3 up to 2 nm. The presence of this layer indicates the efficient relaxation of the large lattice mismatch, \( f_{300}^{500} = \pm 23.4\% \) at the AlN/Si (111) interface.

Generally, it is well known that GaN is not suitable for direct epitaxial growth on Si substrate suffering from a strong tendency towards the formation of amorphous Si₃N₄ when the silicon substrate is exposed to ammonia [93]. Moreover, Ishikawa et al. [94] reported that LT-GaN is not suitable as buffer layer because of the melt-back etching of Si by Ga. Thus, in this study similarly to others (with Amano et al. [31] being the first who used AlN as an intermediate buffer layer between GaN and Si), the insertion of AlN epitaxial layers is used for GaN growth on silicon and serves not only as wetting layers for GaN but also as barrier layers to prevent Ga meltback etching.

![Fig. 5-6: A HRTEM image showing the amorphous layer between the substrate and the AlN-1 layer [92].](image1)

According to Kai Cheng et al. [90], the growth of the AlN epitaxial layers starts with a Volmer-Weber island growth due to the large lattice mismatch between AlN and the Si substrate (17%). In this sample, the first AlN-1 grown layer has a grain-like structure showing a characteristic contrast with bright and dark areas due to a slight misorientation between them.

![Fig. 5-7: (a) A HRTEM image showing the grain-like structure in the AlN-1 layer [92].](image2)
Fig. 5-7: (b) FFT (shown as inset) and filtered IFFT from the area noted with a white rectangular in Fig. 5-7 (a), using only the indicated by the white circles noted as “1” (left image) and by the arrow noted as “2” (right image) [92].

Fig. 5-7: (c) The HRTEM image of (a) showing the grain-like structure in the AlN-1 layer, making clear the origin of the contrast and the growth model. Filtered IFFT results shown in Fig 5-7 (b) are indicated by white curves, disclosing the Volmer-Weber island growth in the AlN-1 layer [92].

An example of this structure is presented in the HRTEM image of Fig. 5-7, making clear the origin of the contrast and the growth model (in (a), (b) and (c)). The Fast Fourier Transform (FFT) of the region marked with a white rectangular in (a) is presented as inset in (b). It is clearly observed in both HRTEM image and FFT, that there exist AlN grains slightly tilted of c-axis. The reconstruction of the lattice fringes via an IFFT using only the indicated by white circles spots (noted as 1) allows the estimation of the tilting angle (as compared to the lattice fringes angle obtained via IFFT using the set of spots noted with arrows (noted as
2). Thus, a typical 8.7 deg. tilted AlN grain is illustrated at Fig. 5-7 (c). On the other hand, there are also regions that are almost c-axis (0001) orientated, indicating that the Si (111) crystal orientation is transferred through the amorphous interlayer to the AlN-1 layer [31].

It is also observed that in the slightly tilted regions, the amorphous interlayer thickness varies as compared to the dimensions and the shape for the perfect oriented ones, probably resulting to this change of crystal orientation. The thickness variation is illustrated in the HRTEM image of Fig. 5-7 (c) with arrows in the amorphous layer, indicating the difference in thickness in the almost c-axis oriented and in the slightly tilted one.

(ii) The high temperature (HT)-AlN/GaN layers

On the top of the AlN-1 layer, a HT-AlN layer is deposited. The already described grain structure extends through the 25nm thick (nominal thickness) AlN-1 into the HT-AlN layer and is responsible for the AlN-1/HT-AlN interface not being very clearly visible [93]. The HRTEM and TEM images shown in Fig. 5-8 and 5-9 respectively present an enhanced contrast making evident that the HT-AlN/GaN interface is highly defective.

It is worth mentioning that many dislocations are observed in the first grown layers, due to the lattice mismatch of the materials. However, as moving towards the structure surface, the situation changes.

Moreover, in order to minimize the misorientation of GaN layer islands grown on top of HT-AlN layer, a smooth surface of HT-AlN is required. According to Kai Cheng et al [90], as the thickness of the AlN epitaxial layer increases, the island density is reduced with the islands size becoming larger. More specifically, with AlN layer thickness reaching 160 nm, the surface is almost smooth and coalesced. In our case, the AlN layer shows an even greater thickness, ranging from 200 nm to 240 nm. As a result, a uniform and almost sharp AlN surface is achieved, being a good template for further AlGaN or GaN growth and thus leading to well orientated GaN islands on top. Indeed, as we will see in the following paragraph, the GaN layer grown on top presents an island growth, probably due to its small thickness, not exceeding the critical for an abrupt surface with fully coalesced islands.
(iii) The AlGaN intermediate layers

In Fig. 5-9, the rough interface between GaN and AlGaN-1 is indicated by white colored arrows, showing the partially coalesced islands formed during growth of the GaN layer in this sample.

![Fig. 5-9: A TEM image showing the HT-AIN/GaN/AlGaN-1 layers. The arrows indicate the interface [92].](image)

The HRTEM image of Fig. 5-10 presents a magnified part of the GaN/AlGaN-1 interface, which has already indicated in the low magnification TEM image of Fig. 5-9 a characteristic roughness.

FFT performed in the area of the HRTEM image of Fig 5-10 (a) is presented in (b). The enlarged part, shown as inset makes clear the existence of double spots and reveals the presence of materials with slightly different lattice constants. According to the theoretical values for the lattice constants for AlGaN-1 (76% Al) and GaN layers (5.024 and 5.189 respectively), the lattice constant ratio towards c-axis, is around 1.032. Taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.043, close enough to the theoretically obtained ratio. The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by no1 and no2 spots represents the areas that give rise to the distinct spots (Fig. 5-10 (c) and (d) respectively). Thus, in this way, the AlGaN-1/GaN interface is highlighted, with the upper part of the HRTEM image of Fig. 5-10 (a) proved to represent the AlGaN-1 layer and the other part on the bottom, GaN layer. However, it must be noted that the interface is not sharp. As already observed in low magnification TEM images, the underlying GaN layer consists of partially coalesced islands. Thus, this fact is obviously expected, due to the rough GaN layer that AlGaN-1 is grown on, which follows the roughness of the underlying layer. Moreover, according to the IFFT results, the non-sharp boundaries of the reconstructed areas (Fig. 5-10 (c) and (d)) indicate an inter-diffusion situation between the two materials.

Furthermore, in the FFT magnified part, presented as inset in Fig. 5-10 (b), a third spot is revealed on the top of the other two, as indicated by the black colored arrow. This spot could represent AlN element, which could be present in the area of Fig. 5-10 (a), due to the inter-diffusion situation. Its presence is supported by the fact that it is positioned closer to the spot no1, with a distance smaller than the distance between spots no1 and no2, which is fully justified by the fact that Al portion in AlGaN-1 is 75%; thus its lattice constant along c-axis is closer to AlN, than to GaN constant.
In order to completely avoid or slow down the compressive stress relaxation rate, three layers of AlGaN with different compositions were introduced, leading to only modest changes in the lattice constant, i.e., the Al content was varied in steps (76%, 35%, 19% Al for the first, second and third grown AlGaN layer respectively). This strain buffer approach results in build-up compressive strain and therefore convex shape of the structure at growth temperatures. After growth process, the wafer is cooled down to the room temperature and its shape becomes concave, as a result of huge difference in thermal expansion coefficient (CTE).
between Si (111) substrate and nitride layers. The intermediate layers tend to relax mostly on interfaces between them, preserving good in-plane structural quality.

In the next figures, typical TEM and HRTEM images reveal the characteristics of the interfaces between the AlGaN intermediate layers. The AlGaN-1/AlGaN-2 interface is indicated by the white colored arrows and the AlGaN-2/AlGaN-3 interface by the red colored arrows in Fig. 5-11 for this sample. More specifically, rough interfaces are observed, with undulations following the rough GaN surface grown on. It is worth mentioning that some of the interfacial roughness was intentionally introduced in order to assist relief during cool down from MOVPE growth temperature of above 1050°C.

![Fig. 5-11: A TEM image showing the intermediate AlGaN layers of the multilayer structure. The arrows indicate the interfaces [92].](image)

In Fig. 5-12, a HRTEM image shows the rough interface between the AlGaN-1 and AlGaN-2 layers, indicated by white arrows.

![Fig. 5-12: A HRTEM image showing the AlGaN-1/AlGaN-2 interface.](image)

The AlGaN-3/GaN interface is clearly of better structural quality as compared to previous grown layers, demonstrating sharp, crack free interfaces. Characteristic TEM and HRTEM images obtained from this sample, shown in Fig. 5-13 (a) and (b) respectively, clearly demonstrate this fact.
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Fig. 5-13: (a) A TEM image showing the interface between the AlGaN-3 and GaN layers. The arrows indicate the interface. (b) A HRTEM image revealing the good quality of the interface [92].

Furthermore, it is clearly evident that the AlGaN intermediate multilayers perform very well to prevent the threading dislocations in the GaN (layer 3) film from propagating into the upper GaN layer (layer 7). As clearly observed in Fig. 5-3, where the whole multilayer structure is shown, dislocations are strongly reduced from the substrate towards the structure surface. The TD density in the AlGaN-2 epilayer is \( \sim 3.5 \cdot 10^{10} \text{cm}^{-2} \) whereas in the upper GaN buffer epilayer is reduced to \( \sim 1 \cdot 10^{10} \text{cm}^{-2} \). Thus, the compositionally graded AlGaN buffers work as a defect filter, making it an effective way to terminate or annihilate dislocations. Similarly to our study, other studies [90], [93], [95] have also shown that AlGaN layers of linearly graded composition can reduce dislocation density. Moreover, resulted structure is free of cracks on the surface, despite the fact that CTE differs almost 2 times between Si and nitride epilayers.

(iv) The GaN layer/LT-AlN interlayer/GaN buffer

The surface morphology of the GaN layer (with thickness around 55-60nm) grown on the step-graded AlGaN intermediate layers is smooth and crack-free, as shown in Fig. 5-14. After the LT-AlN (15-20nm measured thickness) and buffer GaN (>1μm measured thickness) layers growth, the surface of the multilayer buffer structure grown on on-axis Si (111) substrate exhibits even better characteristics (Fig. 5-15): it is extremely sharp and crack free, giving promising results for the following HEMT structure implementation (although as already reported [43], when growing >1μm GaN on Si (111) cracks are observed). As already reported, the use of LT-AlN interlayer in between the GaN layers targets to relieve the tension stress in the GaN buffer films grown on top and thus reduce the cracks in the grown GaN epilayer [96].

Fig. 5-14: A TEM image illustrating the GaN layer surface morphology and the almost sharp LT-AlN layer [92].
**Fig. 5-15:** A HRTEM image showing a magnified part of the upper GaN buffer layer surface, where a smooth and crack-free surface is presented [92].
5.3.2 Multilayer Buffer Structure: Sample #TG1935-4 deg off

Cross-sectional TEM analysis took place for the structural characterization of epilayers and interfaces in this sample too.

Fig. 5-16: A low magnification TEM image showing the buffer multilayer structure grown on 4 deg cut off Si (111) substrate. Contrast changes reveal the layers sequence grown epitaxially on the substrate [92].
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The conventional bright field image in Fig. 5-16 shows the multilayer structure of the specimen grown on Si (111). In the upper part of the structure, the glue indicates the end of the sample. The elemental composition written on the layers is the nominal one, given by the growers (according to the preparation conditions). Moreover, conventional TEM (CTEM) images allow the layers thicknesses measurement. Table 5-3 gives the nominal and experimental thicknesses of the layers concerning the #TG1935 buffer sample (from bottom to top):

<table>
<thead>
<tr>
<th>Layers numbering</th>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
<th>Experimental thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlN-1</td>
<td>25</td>
<td>40-45</td>
</tr>
<tr>
<td>2</td>
<td>AlN-HT</td>
<td>256</td>
<td>215-225</td>
</tr>
<tr>
<td>3</td>
<td>GaN</td>
<td>100</td>
<td>102-106</td>
</tr>
<tr>
<td>4</td>
<td>AlGaN-1 (76% Al)</td>
<td>268</td>
<td>155-163</td>
</tr>
<tr>
<td>5</td>
<td>AlGaN-2 (35% Al)</td>
<td>265</td>
<td>227-233</td>
</tr>
<tr>
<td>6</td>
<td>AlGaN-3 (19% Al)</td>
<td>257</td>
<td>468-479</td>
</tr>
<tr>
<td>7</td>
<td>GaN</td>
<td>100</td>
<td>460-470.4</td>
</tr>
<tr>
<td>8</td>
<td>LT-AlN interlayer</td>
<td>30</td>
<td>12.7-23.3</td>
</tr>
<tr>
<td>9</td>
<td>GaN buffer</td>
<td>1100</td>
<td>1364-1375</td>
</tr>
</tbody>
</table>

Table 5-3: Nominal and experimental layers thickness for sample #TG1935.

Similarly to the previous sample, the electron diffraction study reveals that the layers were grown epitaxially on the Si substrate, besides the small lattice parameters mismatch on the interface plane. A characteristic electron diffraction pattern is shown in Fig. 5-17, obtained from a selected area containing part of the Si substrate and the first layers of Sample-TG1935 (along [Î10] Si). The epitaxial relationships are: the [111] Si direction is parallel to the [0001] AlN direction, the [112] Si direction is parallel to [1100] AlN direction and the [110] Si direction is parallel to [1100] AlN direction.

The main spots of the two phases are indicated with open and dashed circles for Si and AlN respectively.

Fig. 5-17: A typical electron diffraction pattern obtained from a selected area containing Si substrate and the first AlN layers along [110] Si. The very good epitaxial growth of AlN layers on the Si (111) substrate is clear.
In the following paragraphs we discuss the obtained results starting from bottom to top.

(i) The Si substrate/AlN-1 interface

As in the “on axis” situation, in the 4 deg cut off case a thin amorphous interlayer probably SiN$_x$, was revealed by HRTEM at the AlN-1/Si substrate interface (Fig. 5-18), as also mentioned in the work of Kaiser et al. [93]. Similarly to the previous sample, the layers’ thickness is not homogeneous in all areas, varying from around 1 up to 2nm. The presence of this layer indicates the efficient relaxation of the large lattice mismatch $f_{300 K}=+23.4\%$ at the AlN/Si (111) interface. However, in this case, the amorphous layer was observed at some regions at a depth of about 13nm in the Si substrate as well (Fig. 5-19). The insets in this figure represent the FFT transform of the areas indicated by white colored arrows denoting the Si areas surrounding the amorphous layer.

![Fig. 5-18](image)

**Fig. 5-18:** A HRTEM image showing the existence of an amorphous layer in between Si substrate and AlN-1 layer.

![Fig. 5-19](image)

**Fig. 5-19:** A TEM image showing the existence of an amorphous layer in between the Si substrate, inset: FFT indicating the Si areas.

Part of the interface between Si (111) and the amorphous layer is magnified and shown in Fig. 5-20 in higher resolution, where the stepped interface is revealed.
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Fig. 5-20: A HRTEM image showing the interface between Si substrate and the amorphous layer.

The first AlN-1 grown layer presents again a grain-like structure, as previously presented, with the grains exhibiting a slight misorientation from the c-axis. An example of this structure is presented in the HRTEM image of Fig. 5-21, making clear the growth model. The Fast Fourier Transform (FFT) of the region is presented as inset. It is clearly observed in both HRTEM image and FFT, that there exist AlN grains slightly tilted of c-axis. The reconstruction of the lattice fringes via an IFFT using only the indicated by white circles spots allows the estimation of the tilting angle (as compared to the lattice fringes angle obtained via IFFT using the set of spots noted with arrows).

However, in this case, the misorientation angle is close enough to the perfect orientation of c-axis. More specifically, we did not find tilted grains exhibiting more than 2 degrees angle from the perfect c-axis orientation. Moreover, in this case, the amorphous interlayer thickness is more homogeneous as compared to the on axis buffer sample situation [92].

Fig. 5-21: A HRTEM image showing the existence of an amorphous layer in Sample-#TG1924. Moreover, FFT (shown as inset on the left) and filtered IFFT from areas indicated by white curves, disclose the Volmer-Weber island growth in AlN layer.
(ii) The high temperature (HT)-AlN/GaN layers

On the top of the AlN-1 layer, a HT-AlN layer is deposited. In the 4 deg cut off case, due to the almost c-axis oriented grain structure of the AlN-1 layer, the AlN-1/HT-AlN is visible enough as compared to the on-axis case. The HT-AlN layer has a thickness around 220 nm, leading to uniform almost sharp interfaces, and as a result to well orientated GaN islands on top. However, in this sample, due to the fact that GaN layer grown on top of HT-AlN exhibits a thickness greater than in the on axis situation (102-106nm), a uniform and fully coalesced continuous GaN layer is reported (Fig. 5-22). This situation is also presented in the HRTEM image of Fig. 5-23, where the characteristic contrast denotes the GaN/AlGaN-1 interface.

![Fig. 5-22: A TEM image showing the HT-AlN/GaN/AlGaN-1 layers. The arrows indicate the interface [92].](image)

![Fig. 5-23: A HRTEM image showing the almost sharp interface between GaN and AlGaN-1 layers [92].](image)

(iii) The AlGaN intermediate layers

Again, as in the previous sample, three layers of AlGaN with different compositions were introduced, leading to only modest changes in the lattice constant, in order to completely avoid or slow down the compressive stress relaxation rate.

The AlGaN-1/AlGaN-2 (layer 4/layer 5) interface is indicated by the white arrows and the AlGaN-2/AlGaN-3 (layer 5/layer 6) interface by the grey arrows in Fig. 5-24. Almost no interfacial roughness exists in between the AlGaN intermediate layers, as clearly seen in Fig. 5-24. As already mentioned, the GaN/AlGaN-1 (layer 3/layer 4) layers show almost sharp
interface, thus resulting to sharp interfaces of epilayers grown on. Moreover, it is reasonable to conclude that the 4 deg. cut off Si substrate probably results in less interfacial roughness in between the structure than the on-axis one. Finally, the AlGaN-3/GaN (layer 6/layer 7) interface demonstrates a good structural quality of sharp and crack free plane, similarly to the previously deposited layers, as expected.

![TEM image showing sharp AlGaN interfaces](image)

Moreover, many dislocations are observed in the first grown layers, more than in the “on axis” sample, due to the 4 deg cut-off angle. However, as moving towards the structure surface, the situation changes. Indeed, the TD density in the AlGaN-2 epilayer is ~2 \times 10^{10} \text{cm}^{-2} whereas in the upper GaN buffer epilayer is reduced to ~7 \times 10^{9} \text{cm}^{-2}. Thus, it is clearly evident that the AlGaN intermediate multilayers perform very well to prevent the propagation of the threading dislocations from the GaN (layer 3) film into the upper GaN layer (layer 7). As clearly observed in Fig. 5-16 where the whole multilayer structure is shown, dislocations are strongly reduced from the substrate towards the structure surface. Thus, again, it is clearly shown that the compositionally graded AlGaN buffers work as a dislocation filter, producing an effective way to terminate or annihilate dislocations. Similarly to our study, other studies [90], [93], [95] have also shown that AlGaN layers of linearly graded composition can reduce dislocation density. Moreover, resulted structure is free of cracks on the surface, despite the fact that CTE differs almost 2 times between Si and nitride epilayers.

(iv) The GaN layer/LT-AlN interlayer/GaN buffer

In this sample, in the [11\overline{2}0] cut direction, a high density of V-shaped pits (having their end connected with threading dislocations) was observed in GaN layer (grown on the AlGaN-3 layer), which in this case exceeds 450nm thickness, as shown in Fig. 5-25 (probably...
because of strain relaxation reasons). The sides of the pits appear to be aligned with specific crystallographic directions. Considering the growth direction and the angle of the V-pits of about 60°, the sidewalls lie in the \(\{10\bar{1}1\}\) planes. The size of the V-pits varies from 120 up to 230 nm concerning width and from 100 up to 200 nm in depth. The presence of V-pits, initiated by threading dislocations, is probably caused by the increased strain energy and the reduced Ga incorporation on the \([10\bar{1}1]\) pyramid planes as compared to the \([0001]\) plane [97].

However, the cross-section TEM in the \([1\bar{1}00]\) direction elucidated the nature of these defects. The preferential orientation of the defects observed in our samples suggests the presence of a non-uniform strain distribution during the growth of GaN onto off-axis Si substrates, i.e., the strain mainly being relaxed along the \([1\bar{1}20]\) axis.

Most probably, the geometrical configuration of these defects seems like a trench defect, without excluding the presence of V-pits. The term “trench defect” has already been reported by F. C.-P. Massabuau et al. [98]. During the subsequent layer deposition, the overgrown LT-AlN interlayer, with nominal thickness 30nm, “follows” the growth and mounds the underlying V-shaped GaN.

![Fig. 5-25: A TEM image showing the V-shaped formations in the \([1\bar{1}20]\) cut direction [92].](image)

Fig. 5-26 shows in higher resolution the right part of the V-structure presented on Fig. 5-25. FFT performed in the area indicated by the white rectangular is presented on Fig 5-26 (b). The enlarged part, shown as inset makes clear the existence of double spots and reveals the presence of materials with slightly different lattice constants. According to the theoretical values for the lattice constants for AlN and GaN layers (4.997 and 5.189 respectively), the lattice constant ratio towards c-axis, is 1.038. Taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.029, close enough to the theoretically obtained ratio. The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by no1 and no2 spots represents the areas that give rise to the distinct spots (Fig. 5-26 (c) and (d) respectively). Moreover, the bright area (right part of a V structure) of HRTEM image of Fig. 5-26 (a) is proved to be the AlN layer. On the other hand it is clear that the dark areas surrounding the bright one, represent GaN layer. However, it must be noted that the non-sharp boundaries of the GaN reconstructed area (Fig.
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5-26 (d)) indicate an inter-diffusion of the two materials. This is probably the reason of the presence of modulated brightness fringes in nano-areas very close to the AlN layer (Fig. 5-26 (a)).

![Figure 5-26: (a) A HRTEM image showing the right part of V-structure and (b) the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots. (c) IFFT using only the spots noted with 1 that correspond to AlN and (d) IFFT using only the spots noted by 2 that refer to GaN [92].](image)

Subsequently, the GaN buffer layer deposited on the top of LT-AlN interlayer starts growing inside these V-pits, resulting in a very good quality, crack-free smooth layer of 1.3\mu m thickness that can be used as a buffer for the forthcoming growth of the AlGaN/GaN heterostructure for HEMT device application (Fig. 5-27).
5.3.3 Comparison of Samples #TG1934 (on axis) and #TG1935 (4 deg off)

Table 5.4 presents the nominal thickness as well the experimental one for #TG1934 and #TG1935 samples. As clearly observed, the experimental thicknesses of layers concerning both samples show a deviation from the nominal thicknesses reported.

<table>
<thead>
<tr>
<th>Layers Numbering</th>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
<th>Experimental thickness (nm) #TG1934</th>
<th>Experimental thickness (nm) #TG1935</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlN-1</td>
<td>25</td>
<td>238-250*</td>
<td>226.7-231*</td>
</tr>
<tr>
<td>2</td>
<td>HT-AlN</td>
<td>256</td>
<td>43-80</td>
<td>102-106</td>
</tr>
<tr>
<td>3</td>
<td>GaN</td>
<td>100</td>
<td>191-238</td>
<td>155-163</td>
</tr>
<tr>
<td>4</td>
<td>AlGaN-1 (76% Al)</td>
<td>268</td>
<td>195-268</td>
<td>227-233</td>
</tr>
<tr>
<td>5</td>
<td>AlGaN-2 (35% Al)</td>
<td>265</td>
<td>71-265</td>
<td>227-233</td>
</tr>
<tr>
<td>6</td>
<td>AlGaN-3 (19% Al)</td>
<td>257</td>
<td>215-251</td>
<td>468-479</td>
</tr>
<tr>
<td>7</td>
<td>GaN</td>
<td>100</td>
<td>55-58</td>
<td>460-470.4</td>
</tr>
<tr>
<td>8</td>
<td>LT-AlN interlayer</td>
<td>30</td>
<td>17-21</td>
<td>12.7-23.3</td>
</tr>
<tr>
<td>9</td>
<td>GaN buffer</td>
<td>1100</td>
<td>1005-1014</td>
<td>1364-1375</td>
</tr>
</tbody>
</table>

Substrate Si (111):P resistive 675 μm

*It refers to the overall thickness of layers 1 and 2.

Comparing the samples #TG1934 and #TG1935:

First of all, for all the three types of samples the electron diffraction study reveals that the layers were grown epitaxially on the Si substrate, besides the small lattice parameters mismatch on the interface plane. An amorphous layer, believed to be SiNx, with an unhomogeneous thickness, is observed in between the Si substrate and the first grown layer AlN-1, in both samples. This layer existence shows the efficient relaxation of the large lattice mismatch $f_{300K}=+23.4\%$ at the AlN-1/Si (111) interface.

Moreover, in both samples the AlN-1 layer features grain-like growth, due to the Volmer-Weber island growth mode. The AlN layer growth conditions used resulted in almost normal c-plane orientation to the substrate surface regardless of Si (111) tilt; some of the grains are almost c-axis oriented whereas others are slightly misoriented from c-axis. It is also observed...
that in the slightly tilted regions, the amorphous interlayer thickness varies as compared to the dimensions and the shape for the perfect oriented ones, probably resulting to this change of crystal orientation. However, in the “on axis” sample, the misorientation of the grains is greater than in the 4 deg cut-off case. More specifically, we did not find tilted grains with angle exceeding two degrees from the perfect c-axis orientation. Moreover, the amorphous layer thickness is more homogeneous in this case, showing a negligible effect in the misorientation angle. Due to the grain structure, in the case of the “on-axis” sample, the AlN-1/HT-AlN interface is not very clearly visible. This situation is not so obvious in the 4 deg cut-off sample, due to the almost c-axis orientation of grains.

Furthermore, the HT-AlN layer grown on the top of AlN-1 shows an almost sharp surface, being a very good template for the next layers growth, and also minimizing the misorientation of the GaN islands grown on. This GaN layer grown onto the HT-AlN layer presents thickness greater than the critical for island formation, only in the case of the 4 deg cut-off sample. In the “on axis” situation, not fully coalesced island growth is indicated in this GaN layer.

The three intermediate AlGaN layers (AlGaN-1, AlGaN-2, AlGaN-3) grown on top of GaN layer, present rough interfaces, as expected, for the “on axis” sample situation, due to the non-sharp surface grown on. However, the AlGaN-3 as well as the forthcoming GaN layer grown on, present an almost sharp and crack free surface, clearly indicating the effect of the different composition AlGaN layers on the final structure quality. On the other hand, sharp interfaces are observed in the 4 deg cut-off sample. Moreover, these compositionally graded buffer layers were proved to work as a dislocation filter, in both samples (it is important to be referred that the dislocation density was greater in the 4 deg cut-off as compared to the “on axis” case). The upper GaN buffer layer, in the case of 4 deg cut-off, exhibited a reduced value of $\sim 7 \cdot 10^9 cm^{-2}$ TD density, as compared to the value of $\sim 1 \cdot 10^{10} cm^{-2}$ measured in the on axis case.

Moreover, in the 4 deg cut-off sample, the GaN layer (>400nm thickness) grown on the top of the three intermediate layers in the $[\overline{1}1\overline{2}0]$ cut direction features a high density of V-shaped defects (having their end connected to threading dislocations), whereas in the $[\overline{1}100]$ direction no V-defects were observed, resulting in an unhomogeneous strain distribution situation. It is then normal, for the next layers grown (LT-AlN and finally GaN buffer), to start growth into these V-defects. On the other hand, no V-defects where formed in the “on axis” case, with the GaN layer exceeding the 80nm thickness. Most probably, the geometrical configuration of these defects seems like a trench defect. Thus, V-defects formation leads to strain relief only after the GaN film becomes thicker and reaches a critical thickness. As reported, the majority of TDs in GaN-related materials have no driving force to glide at high temperatures, so relaxation via dislocation flow does not exist [99].

Finally, in both “on axis” and 4 deg cut-off samples, a very good quality, crack-free smooth GaN buffer layer of around 1-1.3μm thickness was achieved, used as a buffer for the forthcoming growth of the AlGaN/GaN heterostructure for HEMT device application.
5.3.4 HEMT structure #TG1931-on axis

In this sample, the AlGaN/GaN heterostructure is grown on the top of a buffer structure, similar to the #TG1934 sample buffer structure (on axis). The conventional bright field image of Fig. 5-28, deriving from a combination of TEM images, shows the multilayer structure of the HEMT specimen grown on Si (111). Moreover, Fig. 5-29 shows the left part of Fig. 5-28 magnified, indicating better the presence of nine different layers. The elemental composition noted on the layers is the nominal one, given by the growers (according to the preparation conditions).

Table 5-5 gives the nominal and experimental thicknesses of the layers concerning the TG1931 HEMT sample (from bottom to top). The extra layers grown in this HEMT sample as compared to the previous buffer samples are in bold letters:

<table>
<thead>
<tr>
<th>Layers Numbering</th>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
<th>Experimental thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlN-1</td>
<td>25</td>
<td>263-265*</td>
</tr>
<tr>
<td>2</td>
<td>HT-AlN</td>
<td>256</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>GaN</td>
<td>100</td>
<td>88-111</td>
</tr>
<tr>
<td>4</td>
<td>AlGaN-1 (76% Al)</td>
<td>268</td>
<td>216-223</td>
</tr>
<tr>
<td>5</td>
<td>AlGaN-2 (35% Al)</td>
<td>265</td>
<td>170-244</td>
</tr>
<tr>
<td>6</td>
<td>AlGaN-3 (19% Al)</td>
<td>257</td>
<td>203-247</td>
</tr>
<tr>
<td>7</td>
<td>GaN</td>
<td>100</td>
<td>88-98</td>
</tr>
<tr>
<td>8</td>
<td>LT-AlN interlayer</td>
<td>30</td>
<td>17-23.6</td>
</tr>
<tr>
<td>9</td>
<td>GaN buffer</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>GaN undoped channel</td>
<td>80</td>
<td>1115-1117**</td>
</tr>
<tr>
<td>11</td>
<td>AlN spacer</td>
<td>1</td>
<td>1.6-2.5</td>
</tr>
<tr>
<td>12</td>
<td>AlGaN (~20%Al)</td>
<td>20</td>
<td>19-21***</td>
</tr>
<tr>
<td>13</td>
<td>GaN cap</td>
<td>2-2.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 5-5: Nominal and experimental layers thickness for samples #TG1931.

*The overall thickness of GaN undoped channel and GaN buffer layers is 1.115-1.117μm.

** The overall thickness of HT-AlN and AlN-1 layers is 263-265nm.
***The overall thickness of AlGaN and GaN cap layers is 19-21nm.

**Fig. 5-28:** A low magnification TEM image showing the HEMT multilayer structure grown on “on axis” Si (111) substrate. Contrast changes reveal the layers sequence grown epitaxially on the substrate.

**Fig. 5-29:** A low magnification TEM image showing the HEMT multilayer structure grown on “on axis” Si (111) substrate.
Similarly to the buffer samples, the electron diffraction study in the HEMT sample reveals that the layers were grown epitaxially on the Si substrate, besides the lattice mismatch on the interface plane.

![Electron Diffraction Pattern](image)

**Fig. 5-30:** A typical electron diffraction pattern obtained from a selected area containing Si substrate and the first AlN layers along [110] Si. The very good epitaxial growth of AlN layers on the Si (111) substrate is clear.

A characteristic electron diffraction pattern is shown in Fig. 5-30, obtained from a selected area containing part of the Si substrate and the first layers of Sample-1931. The epitaxial relationships are: the [111] Si direction is parallel to the [0001] AlN direction, the [112] Si direction is parallel to [110] AlN direction and the [110] Si direction is parallel to [1120] AlN direction. The main spots of the two phases are indicated with open and dashed circles for Si and AlN respectively.

In the following paragraphs we discuss the obtained results starting from bottom to top.

(i) The Si substrate/AlN-1 interface

The situation is similar to the “on axis” case of buffer sample #TG1934, where a thin amorphous interlayer probably SiNₓ, was revealed by HRTEM at the AlN-1/Si substrate interface (Fig. 5-31), presenting an unhomogeneous thickness. Again, the presence of this layer indicates the efficient relaxation of the large lattice mismatch $f_{300K} = +23.4\%$ at the AlN/Si (111) interface.

![HRTEM Image](image)

**Fig. 5-31:** A HRTEM image showing the existence of an amorphous layer in between Si substrate and AlN-1 layer.
In this case, similarly to the previous, the first AlN-1 grown layer presents a distorted and grain-like structure showing a characteristic contrast with bright and dark areas due to a slight misorientation between them (Fig. 5-32). Moreover, as already mentioned, in the slightly tilted regions, the amorphous interlayer thickness varies as compared to the dimensions and the shape for the perfect oriented ones, probably resulting to this change of crystal orientation.

![HRTEM image showing the distorted grain-like AlN-1 layer.](image)

(ii) The high temperature (HT)-AlN/GaN/AlGaN intermediate layers

On the top of the AlN-1 layer, a HT-AlN layer (layer 2) is deposited. The already described grain structure extends through the 25nm thick (nominal thickness) AlN-1 into the HT-AlN layer and is responsible for the AlN-1/HT-AlN interface not being very clearly visible. Moreover, in order to minimize the misorientation of GaN layer islands grown on top of HT-AlN layer, a smooth surface of HT-AlN is required. According to Kai Cheng et al [8], as the thickness of the AlN epitaxial layer increases, the island density is reduced with the islands size becoming larger. Furthermore, with AlN layer thickness reaching 160 nm, the surface is almost smooth and coalesced.

![HRTEM image showing the sharp interface between GaN and AlN-HT. The arrows indicate the interface.](image)
In our case, the AlN layer shows an even greater thickness, ranging from 200 nm to 240 nm. As a result, a uniform and almost sharp AlN surface is achieved (as highlighted in the HRTEM image of Fig. 5-33, with the arrows denoting the interface), being a good template for further AlGaN or GaN growth and thus leading to well orientated GaN islands on top.

Fig. 5-34 consists of a combination of images containing part of the multilayer structure (AlGaN-3/AlGaN-2/AlGaN-1/GaN/HT-AlN layers). It is easy to observe non-sharp interfaces between some of the layers. As already mentioned, the HT-AlN exhibits a sharp surface where GaN epilayer is grown on. However, due to GaN thickness (around 88-100nm), islands growth takes place during GaN layer growth (Fig. 5-34), with some areas presenting partially coalesced islands (Fig. 5-35), probably due to a greater thickness.

**Fig. 5-34:** A TEM image showing magnified parts of the AlGaN-3, AlGaN-2, AlGaN-1, GaN, HT-AlN layers.

**Fig. 5-35:** A TEM image showing an area with coalesced GaN islands.
In Fig. 5-36, a HRTEM image shows an example of a rough interface between the GaN and AlGaN-1 layers, with the white colored arrows indicating the interface. However, in order to clearly prove the exact interface position, FFT and IFFT analysis is performed.

![HRTEM image showing the interface between the AlGaN-1/GaN layers.](image)

**Fig. 5-36:** A HRTEM image showing the interface between the AlGaN-1/GaN layers.

The HRTEM image of Fig. 5-37 (a) shows the same AlGaN-1/GaN interface, displaying a wider area though. FFT performed in the area indicated by the white rectangular is presented in Fig 5-37 (b), where the enlarged part, shown as inset, reveals the existence of double spots and thus the presence of materials with slightly different lattice constants. According to the theoretical values for the lattice constants for AlGaN-1 (76% Al) and GaN layers (5.024 and 5.189 respectively), the lattice constant ratio towards c-axis, is around 1.032. Taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.043, close enough to the theoretically obtained ratio. The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by no1 and no2 spots represents the areas that give rise to the distinct spots (Fig. 5-37 (c) and (d) respectively). Thus, in this way, the AlGaN-1/GaN interface is highlighted, with the upper part of the HRTEM image of Fig. 5-37 (a) proved to be the AlGaN-1 layer and the other part on the bottom, GaN layer.

However, it must be noted that the interface is not sharp, showing undulations, as indicated by the white colored arrows noted in Fig. 5-37 (a). As already observed in low magnification TEM images, the underlying GaN layer consists of islands, which in some of the cases are not coalesced at all, in others are partially coalesced. Moreover, according to the FFT (presented as inset in Fig. 5-37 (a)) and IFFT results, the non-sharp boundaries of the reconstructed areas (Fig. 5-37 (b) and (c)) indicate an inter-diffusion of the two materials. This is probably the reason of the presence of modulated brightness fringes in nano-areas very close to the AlGaN-1/GaN interface (Fig. 5-37 (a)).
Chapter 5: Experimental Results

Fig. 5-37: (a) A HRTEM image showing the interface between the AlGaN-1/GaN layers and the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots. (b) IFFT using only the spots noted with 1 that correspond to AlGaN and (c) IFFT using only the spots noted by 2 that refer to GaN.

As moving towards the structure surface, the AlGaN-2/AlGaN-1 interface is again rough, clearly following the GaN surface undulations and forming some kind of V-shapes with dislocations connected to the apex of the V-structures (as shown in the low magnification TEM image of Fig. 5-34). The dislocations pass through the V-shapes and extend to the AlGaN-2 layer, where the majority of them stops propagating. The AlGaN-3/AlGaN-2 interface is also rough, whereas in the AlGaN-3/GaN area the situation is different, where the sharp interface denotes the better surface quality, after the three intermediate layers growth. This situation is clearly observed in the low magnification TEM image of Fig. 5-38, and the HRTEM image of Fig. 5-39.
More specifically, the sharp, crack free AlGaN-3/GaN interface is highlighted in a characteristic HRTEM image shown in Fig. 5-39, where the atomic scale stepped interface is obvious due to the characteristic contrast, as indicated by the arrows. Moreover, two parts of the interface are magnified and presented as insets, showing better the atomic plane steps.

(iv) The GaN layer/LT-AlN interlayer/GaN buffer

Similarly to the buffer sample #TG1934, the surface morphology in this HEMT sample of the GaN layer grown on the step-graded AlGaN intermediate layers is smooth and crack-free, as shown in Fig. 5-40 (indicated by the white colored arrow). After the LT-AlN (layer 8) (15-20nm measured thickness) and buffer GaN (layer 9) (~1μm measured thickness) layers growth, the surface of the multilayer buffer structure grown on “on-axis” Si (111) substrate exhibits even better characteristics (Fig. 5-43 (a)): it is extremely sharp and crack free, giving promising results for the following HEMT structure implementation.
**Fig. 5-40:** A TEM image showing the LT-AlN and GaN layers grown on the AlGaN intermediate layers.

The LT-AlN layer, features almost sharp thickness along the sample, with regions exhibiting a small degree of roughness, as explained through the next HRTEM image of Fig. 5-41.

**Fig. 5-41:** (a) A HRTEM image of the LT-AlN layer and (b) the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots. (c) IFFT using only the spots noted with 1 that correspond to AlN.

More specifically, FFT performed in the area of Fig 5-41 (a) is presented in (b), where the enlarged part, shown as inset, reveals the existence of double spots (indicated by the white colored arrows) and thus the presence of materials with slightly different lattice constants.
According to the theoretical values for the lattice constants for AlN and GaN layers (4.997 and 5.189 respectively), the lattice constant ratio towards c-axis, is around 1.038.

Taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.032, close enough to the theoretically obtained ratio. The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by no1 spot represents the area that give rise to this specific spot (Fig. 5-41 (c)). In this way, the LT-AlN layer is highlighted and the interfaces with the GaN and GaN buffer layer, on the bottom and top respectively, are clearly observed. A small roughness is observed in the GaN/LT-AlN and LT-AlN/GaN buffer interfaces in this case.

(iv) The multilayer structure surface

After the growth of the buffer structure, the AlGaN/GaN heterostructure is finally inserted. Fig. 5-42 presents a TEM image where characteristic undulation is clearly observed.

![Fig. 5-42: A TEM image showing the surface of the multilayer structure - the marked rectangular: magnified part of the AlGaN and GaN layers showing the roughness of the upper GaN layer.](image)

An AlN spacer layer of 1.5-2.5nm thickness was inserted in between the heterostructure, in order to improve the 2DEGs performance [100]. The AlN thickness is almost uniform across the sample, probably giving rise to the electrical characteristics of the electron channel. In Fig. 5-43 (a) and (b), the free surface of this sample is shown, where characteristic and periodic undulations (V-pits) are revealed, with a height of around 15nm. The GaN-cap layer (indicated by arrows in Fig. 5-43 (b)), which is not always clearly visible, follows these V-pits of the AlGaN layer.
Fig. 5-43: (a) A HRTEM image showing a magnified part of the upper layers, (b) A HRTEM image showing the surface V-pits. The arrows indicate the GaN cap layer, although not clear enough [92].

However, in some areas, the GaN-cap layer does not seem to completely follow the AlGaN layer roughness, forming some new V-shaped areas. This fact is clearly presented in Fig. 5-44.

Fig. 5-44: (a) A HRTEM image showing the surface V-pits and (b) the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots. (c) IFFT using only the spots noted with 2 that correspond to GaN.

More specifically, FFT performed in the area of Fig 5-44 (a) is presented in (b), where the enlarged part, shown as inset, reveals the existence of double spots (indicated by the white colored arrows) and thus the presence of materials with slightly different lattice constants.
According to the theoretical values for the lattice constants for AlGaN (around 20%) and GaN layers (3.13 Å and 3.19 Å respectively), the lattice constant ratio towards [1\(\bar{1}00\)], is around 1.019.

Taking into account the FFT results, the distance of each one of the double spots gives a ratio equal to 1.012, close enough to the theoretically obtained ratio. The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by no2 spot represents the area that give rise to this specific spot (Fig. 5-41 (c)). In this way, the GaN layer is highlighted, which in this case, forms V-shapes on the already V-shaped AlGaN barrier layer.

As already reported [22], [101], [102], in order to obtain a maximal electron density in the 2DEG electron channel any relaxation of the top Al\(_{0.2}\)Ga\(_{0.8}\)N should be avoided. The onset of relaxation is determined by the strain via the Al content of the Al\(_{x}\)Ga\(_{1-x}\)N layer and by the thickness of this layer [103]. In our case, although the low Al concentration (20%) should lead to uniform surface, TEM study showed V-shaped defects on the top of the structure. This phenomenon could be attributed to the thickness of the upper layer (19-21 nm), probably exceeding the critical relaxation thickness. Thus, there is a certain critical layer thickness of the Al\(_{x}\)Ga\(_{1-x}\)N at which relaxation and stress reduction sets in, regardless of the presence of low Al content. Generally, in polar c-plane growth of III-Nitrides, V-defects (i.e. V-shaped surface pits) have been observed and have been shown to be the result of surface relaxation around threading dislocations (TDs) with c-type Burgers vector components. In the case of semipolar growth orientation of III-Nitrides, these V-defects are also connected to TDs (but of mixed type) [104].
Chapter 6: Experimental results
Heterostructures grown on SiC substrates

6.1 Introduction

Wide band gap semiconductors (SiC and GaN), offer great advantages, making them ideal candidates for high power and frequency applications: they combine a wide band gap, a high breakdown field (over 3.75 MV/cm for GaN), a high saturation velocity and they possess the ability to form high quality AlGaN/GaN heterostructures with good transport properties [105], [106].

A typical example of a promising high performance application of GaN-based devices is the use of the AlGaN/GaN heterostructure in high electron mobility transistors (HEMTs). More specifically, the aluminum gallium nitride (AlGaN)/GaN compound system exhibits a large band gap (GaN 3.4 eV, aluminum nitride (AlN) 6.2 eV), a high saturated drift velocity of electrons (2.2x10^7 cm/s), a high breakdown electric field (1–3x10^10 V/cm) and good thermal stability properties [107]. These properties make this system an ideal candidate for electronic and optoelectronic applications. Moreover, the large conduction band discontinuity and strong spontaneous and piezoelectric polarization effect that it presents, induce a 2-dimensional electron gas (2DEG) near the interface (without any intentional doping), making it ideal for HEMT implementation [84].

Due to the fact that native substrates of GaN are still very expensive [108], the growth of GaN and related materials is mostly carried out on various foreign substrates such as sapphire (α-Al₂O₃), silicon (Si) and silicon carbide (SiC) [109]. Because of the availability and relatively low cost characteristics, GaN-based devices are normally grown on sapphire substrates. However, their lattice parameter and coefficient of thermal expansion (TEC) present a significant difference as compared to that of GaN.

For power device applications, however, SiC is the most suitable substrate for GaN heteroepitaxy, exhibiting many interesting properties surpassing those of sapphire or silicon: A higher thermal conductivity (3.7 W/(cm-K)) (almost one order of magnitude greater than that of sapphire) and a lower lattice mismatch to GaN (about 3.4%) and AlN (<1%) [110]. It must be taken into account though that even this relatively small lattice mismatch combined with the TEC mismatch can result in crystalline defects and bowing of the epitaxial wafers, degrading the device performance. A usual problem that occurs during growth of GaN directly on (0001) SiC substrates is that GaN is under tensile strain, resulting in a high dislocation density and even cracks in the GaN epilayer.

Moreover, many studies have already been conducted to the growth of GaN-based electronic devices on off-axis SiC. Indeed, as the SiC substrate size has already reached 6-inch, even 4-deg off-cut increases significantly the wafers cost [111]. Therefore, nowadays the research is directed to the growth of AlGaN/GaN heterostructures onto 2 degrees off axis
4H-SiC substrates in order to significantly reduce the waste material during boule cutting process.

In the next paragraphs, we report on the structural characterization of AlGaN/GaN heterostructures grown on 4H-SiC (0001) substrates by metalorganic vapor phase epitaxy (MOVPE) method. Two types of substrates were used: on axis and 2-deg cut off. The structural characterization was performed by using conventional and high-resolution Transmission Electron Microscopy (TEM and HRTEM) as well as advanced microscopy techniques (Scanning Transmission Electron Microscopy-STEM, combined with Energy Dispersive X-ray-EDX analysis).

### 6.2 Experimental

#### 6.2.1 Sample Preparation

The surface of the SiC substrate is important to be polished, in order to achieve a high quality epitaxial growth on it. In this work, chemical-mechanical planarization process (CMP) has been applied before growth, for mirror-like surfaces and excellent surface roughness [112]. As reported, the surface quality concerns the flatness, the sub-surface dislocations and the residual stress. In order to suppress defect generation during initial steps of epitaxial growth, a stress-free surface with no sub-surface dislocations is indispensableness [113].

The epitaxial growth of the multilayer structures on (0001) SiC substrate was carried out using EMCORE Turbodisc™ D75 metalorganic chemical vapor deposition (MOCVD) system operating at low pressures. Trimethylgallium (TMG), trimethylaluminum (TMA), and ammonia (NH3) were used as Ga, Al and N precursors, respectively. Before the growth initiation, the substrates were subjected to a thermal cleaning in flowing H2 using T>1100°C, in order to clean the Si-surface of the hexagonal SiC. After that, the temperature was reduced to ~1000°C at ~100mbar absolute pressure and ammonia was introduced into the reactor. Thus, surface got nitridated for a short time. Finally, the introduction of the Aluminum precursor (TMAI) took place and growth started.

At first, an AlN nucleation layer was deposited, on which the AlGaN/GaN heterostructure was grown in sequence of a GaN buffer layer and an AlGaN (21% Al) barrier layer. An extra AlN spacer layer was deposited in between the AlGaN/GaN heterostructure. Finally, a GaN cap layer was grown on the top of the HEMT structure. All layers were grown with unintentional doping.

Two sets of samples were grown on Si-face CMP 4H-SiC (#TG1929-on ±0.5 deg off (4H), #TG2135-on 2 deg off (4H)) and one on Si-face CMP 6H-SiC (#TG2134-on 1 deg off (6H)). The epi-structures consisted of AlN nucleation layer, GaN buffer, GaN undoped, thin AlN spacer, AlGaN and GaN cap layers (as observed in CTEM and HRTEM images shown below). The structure of the samples is shown schematically in Fig. 6-1.
The expected nominal and measured thicknesses for samples grown on 4H-SiC and 6H-SiC are noted in Tables 6-1 and 6-3 respectively (bottom to top).

<table>
<thead>
<tr>
<th>Layers Numbering</th>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlN nucleation layer</td>
<td>60-90</td>
</tr>
<tr>
<td>2</td>
<td>GaN buffer</td>
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<tr>
<td>3</td>
<td>GaN undoped channel</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>AlN spacer</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>AlGaN (~20%Al)</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>GaN cap</td>
<td>2-2.5</td>
</tr>
</tbody>
</table>

Table 6-1: Nominal thicknesses for the structures grown on 4H-SiC substrate.

Moreover, in Table 6-2, the XRD results (thickness and Al content of AlGaN layer) of the structures grown on 4H-SiC substrate (on-axis and 2 deg cut off) are summarized and compared with the TEM results (which will be reported in the next paragraphs). It is obvious
that there is no significant difference, although the exact thickness of the structure is accurately measured and presented using TEM observation results. Concerning the elemental composition of all layers, the STEM-EDX (Scanning Transmission Electron Microscopy-Energy Dispersive X-ray Spectrometry) analysis that follows in the next chapters will give precise results.

<table>
<thead>
<tr>
<th>Layers Numbering</th>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlN nucleation layer</td>
<td>60-90</td>
</tr>
<tr>
<td>2</td>
<td>GaN buffer</td>
<td>1720</td>
</tr>
<tr>
<td>3</td>
<td>GaN undoped channel</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>AlN spacer</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>AlGaN (~20%Al)</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>GaN cap</td>
<td>2-2.5</td>
</tr>
</tbody>
</table>

6H-SiC Substrate

Table 6-3: Nominal thicknesses for the structure grown on 6H-SiC substrate.

The structural characterization of the MOVPE-grown specimens was carried out using a JEOL 2011 system operated at 200 keV. Z-Contrast imaging and compositional analysis of layers and interfaces was carried out combining STEM-HAADF (High Angle Annular Dark Field) and STEM-EDX (Energy Dispersive X-ray Spectrometry) methods. TEM specimens were prepared using traditional methods, as for example described in [91].
6.3 TEM results-Sample #TG1929 (± 0.5 deg off)

In Table 6-4 the nominal and experimental thicknesses of the multilayer structure are presented:

<table>
<thead>
<tr>
<th>Layers numbering</th>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
<th>Experimental thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlN nucleation layer</td>
<td>60-90</td>
<td>14-35</td>
</tr>
<tr>
<td>2</td>
<td>GaN buffer</td>
<td>1720</td>
<td>1827-1849*</td>
</tr>
<tr>
<td>3</td>
<td>GaN undoped channel</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>AlN spacer</td>
<td>1</td>
<td>1.5-3.5</td>
</tr>
<tr>
<td>5</td>
<td>AlGaN (~20%Al)</td>
<td>20</td>
<td>22.3-30.8**</td>
</tr>
<tr>
<td>6</td>
<td>GaN cap</td>
<td>2-2.5</td>
<td></td>
</tr>
</tbody>
</table>

*It refers to the overall thickness of layers 2 and 3

**It refers to the overall thickness of layers 5 and 6.

For all samples the electron diffraction study reveals a strong epitaxial relationship between the epilayers and the 4H-SiC substrate, besides the lattice mismatch on the interface plane. A typical example is shown in Fig. 6-2, obtained from a selected area containing part of the 4H-SiC substrate and the first grown layers. The following epitaxial relationships are deduced:

\[
[0001]_{4H-SiC}//[0001]_{GaN}, [\bar{1}1\bar{0}0]_{4H-SiC}//[1\bar{1}00]_{GaN} \text{ and } [11\bar{2}0]_{4H-SiC}//[11\bar{2}0]_{GaN}
\]

The main spots of the two phases are indicated by arrows.

According to the theoretical 4H-SiC, AlN and GaN unit cell parameters (Table 6-5), the AlN spots can be highlighted in the triple spot areas observed in the electron diffraction pattern. More specifically, an example is presented as inset, where a magnified part clearly reveals the triple area spots, and thus the AlN spot.

<table>
<thead>
<tr>
<th></th>
<th>4H-SiC</th>
<th>AlN</th>
<th>Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>3,0617</td>
<td>3,099</td>
<td>-1,22%</td>
</tr>
<tr>
<td>b (Å)</td>
<td>3,0617</td>
<td>3,099</td>
<td>1,20%</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10,053</td>
<td>4,997</td>
<td></td>
</tr>
<tr>
<td>c/6=c/2=2,51325</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6-5: Unit cell parameters of 4H-SiC and AlN and deviation %.
Fig. 6-2: (a) Typical electron diffraction pattern taken along [11\(\overline{2}\)0] SiC close to 4H-SiC/GaN interface, revealing the very good epitaxial growth of GaN on the 4H-SiC substrate. A magnified part of the diffraction pattern (noted with a white colored rectangular) is presented as inset, revealing the AlN spot.
Chapter 6: Experimental results

Fig. 6-3: A low magnification TEM images showing the multilayer structure grown on (0001) 4H-Si substrate for sample #TG1929. Contrast changes reveal the sequence of layers grown epitaxially on the substrate.

The conventional bright field image of Fig. 6-3 presents the multilayer structure grown on 4H-SiC. In this image, defects -mostly dislocations- are observed, beginning from the AlN/GaN interface and expanding towards the structure surface. As widely reported [115], the majority of the TDs observed in the AlN and GaN layer are a-type. The TD density in the GaN layer is \( \sim 9 \cdot 10^9 \text{cm}^{-2} \). Closed dislocation loops are observed in the GaN layer, noted with arrows in Fig. 6-3. According to other studies [116], a significant fraction of TDs bend into the basal plane and react with dislocations of the opposite phase, and are eliminated by forming closed loops in the lower regions of the GaN epilayer.

Generally, as we move towards the structure surface, dislocations sharply decrease, indicating a higher crystal quality GaN epilayer. Obviously, a high crystalline quality of the epilayers will be advantageous to a better AlGaN/GaN heterostructure and thus device performance [110].

In order to reveal the characteristics of each one of the layers of the multilayer structure, higher magnification TEM observations are essential. Thus, in the following paragraphs we discuss the obtained results starting from bottom to top.
6.3.1 The effect of the AlN nucleation layer

Cross-sectional TEM analysis was carried out in order to study the structure of the first grown AlN nucleation layer. In Fig. 6-4, the AlN nucleation layer is shown in low magnification. This layer is full of structural defects. Also the dislocations starting from the AlN/GaN interface are more obvious in this image. Moreover, the AlN layer thickness does not exceed 40nm. Although it is too thin to accommodate the stress induced due to TEC mismatch, no cracks are observed in the epilayers.

The use of an AlN buffer layer has been widely used to reduce the tensile strain, important for a smooth GaN layer surface with a low threading dislocations density grown by MOCVD method. More specifically, as reported by Lahreche et al. [117], the growth of GaN directly on SiC substrate, results in a rough, islanded GaN layer due to poor surface wetting, deteriorating the GaN film quality. For this reason, L. Lie et al. have reported the use of an AlN buffer layer, prior to GaN growth, being a good wetting agent on the SiC substrate [118]. Moreover, the use of the AlN layer before GaN growth serves as an intermediate layer with smaller lattice mismatch with SiC (reducing it from -3.9% to -2.4%).

![TEM image showing the first grown AlN nucleation layer.](image)

6.3.2 V-shaped structures in AlN nucleation layer

As shown in the TEM images of Fig. 6-5, the AlN nucleation layer at a thickness of about 35 nm is composed of flat-topped partially coalesced V-shaped structures with random shapes. The V-shapes present an angle of about 60°, with their sides aligned with specific crystallographic directions ([10\overline{1}1] sidewalls). V-shapes widths of 20-45 nm with a depth around 20-25nm are observed.

According to [119], the V-pits seem to have grown laterally and vertically with different growth rates, with a higher vertical as compared to the lateral-sidewalls growth rate. More specifically, a reduced Al incorporation (and thus growth rate) on the reversed pyramid walls ([10\overline{1}1]) in comparison with the (0001) planes could have resulted in this defect formation [119]. The V-pits could be formed either by threading dislocations [120]–[122] or by basal stacking faults connected to stacking mismatch boundaries [123].

Several other authors have investigated the structure of similar V-shaped structures that can be formed in GaN-based heterostructures. Bai et al. [124] proposed that the V-shaped pits...
were formed during the growth interruption between AlN and GaN growth due to etching by H₂. However, only the H₂ etching effect couldn’t explain the pit generation in the wafers of Cho et al. [47], so it was concluded that the formation of them is strongly related with AlN surface morphology. Liliental-Weber et al. [125] suggested that V-pits can originate from positions where the surface becomes rougher during growth, for example at the growth front where islands meet each other. Smart et al. [126] reported that pits and undulations on the surface of an AlN buffer layer can result from polishing scratches in the SiC substrate.

![Image](image.jpg)

**Fig. 6-5:** A TEM image showing the formations in the AlN nucleation layer.

A characteristic HRTEM image showing a characteristic V-shape is presented in Fig. 6-6 (a). FFT performed in the area indicated by the white rectangular is presented on Fig 6-6 (b). The enlarged part, shown as inset, makes clear the existence of double spots and reveals the presence of materials with slightly different lattice constants. According to the theoretical values for the lattice constants for AlN and GaN layers (4.997 and 5.189 respectively), the lattice constant ratio towards c-axis, is 1.038. Taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.035, close enough to the theoretically obtained ratio. The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by no1 and no2 spots represents the areas that give rise to the distinct spots (Fig. 6-6 (c) and (d) respectively). Thus, the area inside the V-pit shown in the HRTEM image of Fig. 6-6 (a) is proved to be the GaN layer. On the other hand it is clear that the areas surrounding it, represent AlN layer. However, it must be noted that the non-sharp boundaries of reconstructed areas in Fig. 6-6 (c) and (d) indicate an inter-diffusion of the two materials. This is probably the reason of the presence of modulated brightness fringes in areas in the V-structure walls (Fig. 6-6 (a)).
Fig. 6-6: (a) A HRTEM image showing the right part of V-structure, (b) the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots. (c) IFFT using only the spots noted with the arrow that correspond to GaN, (d) IFFT using only the spots noted with no2 that refer to AlN.

Furthermore, in order to precisely determine the chemical composition of the elements, a STEM-HAADF combined with STEM-EDX analysis is essential, for Z-contrast imaging and chemical mapping of the V-shaped structures area respectively. The STEM-EDX analysis is presented in Chapter 7.

In addition, an almost smooth surface of the overgrown GaN was observed. Due to the thick GaN layer (1.6-1.8 μm thick) grown over AlN, the initially isolated GaN islands coalesced resulting in this smooth surface. Similarly to this study, R. Davis et al. [127] and Nishida et al. [128] have observed that the GaN layer grown on AlN buffer layers exhibits similar surface features as the layer on which they are grown to and that the preferential nucleation sites of GaN islands are the undulations-pits of the AlN surface.
Finally, only few steps are observed in the 4H-SiC/AlN interface, corresponding to the almost on-axis substrate surface.

### 6.3.3 Surface of multilayer structure

After the thick GaN buffer layer growth, the GaN/AlGaN heterostructure is deposited, with an AlN spacer layer grown in between. By magnifying the upper part of the structure of TEM image of Fig. 6-3, the free surface of the specimen is clearly seen. In the TEM and HRTEM images of fig. 6-7 and 6-8 respectively, the surface of Sample #TG1929 is shown. The presence of glue indicates the end of the sample. In this case, where the structure is grown on an almost on axis substrate, the free surface of the specimen appears a characteristic undulation forming V-shaped defects.

**Fig. 6-7:** A TEM image showing the modulation existing in the free surface of the onaxis sample.

**Fig. 6-8:** A HRTEM images showing the surface of the multilayer structure for Sample #TG1929, showing V-shaped formations.

The low Al concentration of the AlGaN layer (21%, less than 25%), should lead to smooth AlGaN surfaces [129]. However, unlike Cho et al. study [129] for the Al\textsubscript{0.21}Ga\textsubscript{0.79}N/GaN on axis sample, the surface of the Al\textsubscript{0.21}Ga\textsubscript{0.79}N layer shows many periodic V-shaped defects.
The size of these formations is small, with an average diameter of 5 nm and an average height of 6 nm each. The angle of the sidewalls is around 110°. Moreover, the presence of the defects can be attributed to the fact that the AlGaN layer thickness (together with the GaN cap layer - not clearly visible in our TEM images, which has a nominal thickness of 2-2.5 nm) is 22.3-30.8 nm. As a result, the AlGaN layer thickness exceeds the critical thickness and so V-shaped defects are created for strain relaxation reasons. Actually, the critical thickness is exceeded due to combined action of AlN spacer with AlGaN and GaN cap layers. According to other studies, the origin of these defects could be threading dislocations [120]–[122] or basal stacking faults (BSF) combined with stacking mismatch boundaries (SMB) [123].

As already reported [22], it is important to obviate any AlGaN relaxation, for a maximal electron density achievement in the 2DEG channel, determined by the strain via the Al content of the AlGaN layer and by the thickness of this layer. In this way, after a certain critical AlGaN thickness, relaxation and stress reduction will set in, negatively affecting the 2DEG density and also the sheet resistance [103].

### 6.3.4 The effect of the AlN spacer layer

In the studied samples, similarly to previous works [130], a thin AlN spacer layer (with nominal thickness 1 nm) was inserted after the growth of GaN and prior to the growth of AlGaN barrier layer in order to enhance the heterostructure interface and improve the electrical properties of the structure.

The HRTEM image of Fig. 6-9 (a) reveals the growth of the AlN spacer layer in between the AlGaN/GaN heterojunction. It is clearly seen that this layer does feature an almost uniform thickness and clear interfaces with the AlGaN and GaN layers [131], although the measured AlN thickness in some of the cases reaches ~3.5 nm exceeding the nominal one (1nm). A future electrical characterization study could clearly determine the electronic properties of the 2DEG formed in the AlGaN/GaN heterostructure and the effect of the AlN spacer layer presence. As already reported by I.P. Smorchkova et al. [130], the growth of a thin (~1nm) AlN layer between AlGaN (x~0.2-0.45) and GaN with thick AlGaN barrier layers (~20-25nm) does not affect the 2DEG sheet density but results in a low-temperature electron mobility values increase.

FFT performed in the area indicated by the white rectangular noted in Fig. 6-9 (a) is presented on Fig. 6-9 (b). The enlarged part, shown as inset, makes clear the existence of double spots and reveals the presence of materials with slightly different lattice constants. According to the theoretical values for the lattice constants for AlN and GaN layers (4.997 and 5.189 respectively), the lattice constant ratio towards c-axis, is 1.038. Taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.04, close enough to the theoretically obtained ratio.
Fig. 6-9: (a) A HRTEM image showing the GaN/AlN/AlGaN heterostructure, (b) the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots. (c) IFFT using only the spots noted with no1 that correspond to GaN and (d) IFFT using only the spots noted with no2 that refer to AlN. (e) IFFT using only the spots noted with no3 that probably represent AlGaN.

The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by no1 and no3 spots represents the areas that give rise to the distinct spots (Fig. 6-9 (c) and (e) respectively). Moreover, the bright area of HRTEM image of Fig. 6-9 (a), which according to growth conditions indicates the AlN spacer layer, is indeed proved to be AlN layer (corresponding to spot no3 on FFT). On the other hand, it is clear that the surrounding areas, represent GaN layer. However, it must be noted that the non-sharp boundaries of the GaN reconstructed area (Fig. 6-9 (c)) indicate an inter-diffusion of the two materials. This is probably the reason of the presence of modulated brightness fringes in areas very close to the AlN layer (Fig. 6-9 (a)). Finally, using the spot indicated by no2 in the FFT (Fig. 6-9 (b)), which is placed in between spots no1 and no3, the reconstruction of the lattice fringes via IFFT is shown in Fig. 6-9 (d), representing an area on the upper part of the AlN spacer layer, but without having clear interfaces and presenting an inter-diffusion situation. This area could represent the AlGaN layer, since the spot corresponding to this material is found to be in between the spots corresponding to GaN and AlN in the FFT results. This fact is consistent with the fact that the lattice parameters of AlGaN material have values in between the values for GaN and AlN ones.
6.3.5 The GaN cap layer

As already reported, any surface steps, charges and traps formed due to dangling bonds as well as any threading dislocations reaching the AlGaN barrier layer surface, can be easily reduced by passivating the surface [132]. One way to passivate the surface is to use a thin enough GaN layer used as a cap layer on the top of the AlGaN epilayer [133]. In order to improve HEMT device quality, the surface near the 2DEG, which controls the 2DEG channel density, must present the lower possible defect states.

In our case, the upper GaN cap layer, grown for passivation reasons, with a thickness not exceeding the 3nm, exhibits similar features and follows the morphology of the AlGaN layer grown onto.

6.4 TEM results-Sample #TG2134 (1 deg off)

In Table 6-6, the nominal and experimental thicknesses of the multilayer structure grown on 1 deg cut off 6H-SiC substrate are presented:

<table>
<thead>
<tr>
<th>Layers numbering</th>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
<th>Experimental thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlN nucleation layer</td>
<td>60-90</td>
<td>13-33</td>
</tr>
<tr>
<td>2</td>
<td>GaN buffer</td>
<td>1720</td>
<td>1680-1700*</td>
</tr>
<tr>
<td>3</td>
<td>GaN undoped channel</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>AlN spacer</td>
<td>1</td>
<td>2-4</td>
</tr>
<tr>
<td>5</td>
<td>AlGaN (~20%Al)</td>
<td>20</td>
<td>20-21**</td>
</tr>
<tr>
<td>6</td>
<td>GaN cap</td>
<td>2-2.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 6-6: Nominal and measured thicknesses for the structures grown on 6H-SiC substrate.

*It refers to the overall thickness of layers 1 and 2.

**It refers to the overall thickness of layers 5 and 6.

The electron diffraction study reveals a strong epitaxial relationship between the epilayers and the 6H-SiC substrate, besides the lattice mismatch on the interface plane. A typical example is shown in Fig. 6-10, taken along [11\overline{2}0] SiC. It is clear for the epitaxial relationships that the [0001] SiC direction is parallel to the [0001] GaN direction, the [\overline{1}100] SiC direction is parallel to [1\overline{1}00] GaN direction and the [11\overline{2}0] SiC direction is parallel to [11\overline{2}0] GaN direction. The main spots of the two phases are indicated with arrows, pointing to the right for GaN and to the left for SiC.
According to the theoretical 6H-SiC, AlN and GaN unit cell parameters (Table 6-7), the AlN spots can be easily highlighted in the triple spot areas observed in the electron diffraction pattern. More specifically, an example is presented as inset, where a magnified part clearly reveals the triple area spots, and thus the AlN spot.

<table>
<thead>
<tr>
<th></th>
<th>6H-SiC</th>
<th>AlN</th>
<th>Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>3,0617</td>
<td>3,099</td>
<td>-1,22%</td>
</tr>
<tr>
<td>b (Å)</td>
<td>3,0617</td>
<td>3,099</td>
<td>1,20%</td>
</tr>
<tr>
<td>c (Å)</td>
<td>15,1183</td>
<td>4,997</td>
<td></td>
</tr>
<tr>
<td>c/6</td>
<td>2,51972</td>
<td></td>
<td>0,84%</td>
</tr>
<tr>
<td>c/2</td>
<td>2,4985</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 6-7: Unit cell parameters of 6H-SiC and AlN and deviation %.*

Fig. 6-10: A typical electron diffraction pattern taken along [11\(\bar{2}\)0] SiC close to 6H-SiC /GaN interface, revealing the very good epitaxial growth of GaN on the 6H-SiC substrate.

For the structural characterization of the epilayers and interfaces cross-sectional TEM analysis was carried out. The low magnification image of Fig. 6-11 shows the multilayer structure grown on the 1 deg off 6H-SiC substrate. In the upper part of the structure, the glue used for the preparation of the samples, clearly indicates the end of the sample.

In this TEM image, the presence of defects -mostly dislocations- that begin from the AlN/GaN interface and expand towards the surface of the structure are observed. However,
the dislocations density is smaller than in the on axis sample case, probably due to strain relaxation reasons [134], [135].

Moreover, as we move towards the structure surface, dislocations sharply decrease, indicating a higher crystal quality GaN epilayer. Obviously, a high crystalline quality of the epilayers will be advantageous to a better AlGaN/GaN heterostructure and thus device performance [110].

Fig. 6-11: A low magnification TEM image showing the multilayer structure grown on 6H-SiC substrate.

The conventional bright field image cannot show the entire multilayer structure on 6H-SiC as seen in Fig. 6-11, and so higher magnification is needed. Thus, in the following paragraphs, magnified parts of the multilayer structure are presented, revealing better the features of the layers (from bottom to top).
6.4.1 The effect of the AlN nucleation layer

In the bright field TEM image of Fig. 6-12, the first grown AlN nucleation layer is shown. This layer exhibits a thickness not exceeding 40nm and it is full of structural defects. More specifically, some dislocations appear starting from the AlN/GaN interface and move towards the structure surface. However, as already referred in this case, the dislocations density is smaller than in the on axis sample.

![Fig. 6-12: A Bright Field (BF) TEM image showing the AlN nucleation layer.](image)

V-shaped defects are formed into the AlN nucleation layer. A characteristic HRTEM image shows the GaN/AlN nucleation layer area, as presented in Fig. 6-13. A Fast Fourier Transform (FFT) performed in the area indicated by the white rectangular is presented on Fig. 6-13 (b). The enlarged part, shown as inset, makes clear the existence of double spots and reveals the presence of materials with slightly different lattice constants.
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Fig. 6-13: (a) A HRTEM image showing the right part of V-structure, (b) the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots. (c) IFFT using only the spot noted with the arrow that corresponds to GaN.

According to the theoretical values for the lattice constants for AlN and GaN layers (4.997 and 5.189 respectively), the lattice constant ratio towards c-axis, is 1.038. Taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.03, close enough to the theoretically obtained ratio. The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by the arrow spot represents the areas that give rise to the distinct spot (Fig. 6-13 (c)). Thus, the area inside the V-structure is proved to be the GaN layer. On the other hand it is clear that the rest area, represents the AlN layer. However, it must be noted that the non-sharp boundaries of the GaN reconstructed area (Fig. 6-13 (c)) indicate an inter-diffusion of the two materials. This is probably the reason of the presence of modulated brightness fringes in areas very close to the AlN layer (Fig. 6-13 (a)).

6.4.2 6H-SiC/AlN nucleation layer interface

Few steps are revealed in the 6H-SiC/AlN interface. A typical example of an atomic scale step is noted in Fig. 6-14, where the dotted line determines the interface between the AlN nucleation layer and the 6H-SiC substrate. The white colored rectangular defines the unit cell of 6H-SiC.
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In the next HRTEM image (Fig. 6-15) white colored arrows indicate the steps’ positions in the 6H-SiC/AlN interface. Characteristic contrast suggests the growth of threading dislocations in the AlN layer that begin from the 6H-SiC/AlN interface at the steps’ positions. The surface of the 6H-SiC substrate consists of (0001) atomically flat and smooth terraces and mostly one atomic layer steps (0.25nm height). Moreover, the steps are perpendicular to [1120] direction (or aligned along [1̅100] direction) and the distance between the steps (length of terraces) of about 15 nm is found to almost correspond to the 1 deg off-cut.

Fig. 6-15: A HRTEM image showing the steps’ positions and the defect formation in the 6H-SiC/AlN interface.

Fig. 6-16 (a) shows a specific part of the HRTEM image of Fig. 6-15, where a characteristic defect formed at the step position marked with the horizontal arrow is magnified.
Fig. 6-16: (a) A HRTEM image showing a magnified part of the HRTEM image of Fig. 6-15, presenting a defect formed in the step position (marked with an horizontal arrow). The FFT is presented as inset. (b) A Filtered IFFT of the area shown in (a), with the mask noted on the FFT of (a). A magnified part of the IFFT is presented as inset, where a dislocation is noted with an arrow ($g=[0002]$, $g=[0004]$). (c) A Filtered IFFT of the area shown in (a), with the mask noted on the FFT of (a). A magnified part of the IFFT is presented as inset, where a dislocation is observed ($g=[1\bar{1}00]$).

A Fast Fourier Transform (FFT) performed in the area shown in Fig. 6-16 (a) is presented as inset. The reconstruction of the lattice fringes via a filtered IFFT using only the indicated by the open circles spots represents the areas that give rise to these spots, and more specifically the horizontal lattice fringes (Fig. 6-16 (b)). A magnified part of the IFFT is presented as inset, where a dislocation is noted with an arrow ($g=[0002]$, $g=[0004]$). Moreover, a stacking fault exists in the upper part of the enhanced contrast (contrast which indicates the presence of a defected-strained area) in Fig. 6-16 (a). In Fig. 6-16 (c), by using only the set of spots marked with an open rectangular, the IFFT results show dislocations-like defects ($g=[1100]$). These kind of vertical defects are formed between differently stacked
domains on the left and right side of the step (called stacking mismatch boundaries), as extensively discussed in Chapter 7 (paragraph 7.2.2).

Moreover, stacking mismatch boundaries (SMBs) that are formed in the steps of the SiC/AlN interface, can easily initiate the V-shaped defects. More specifically, a model proposed by Cho et al. [136] properly customized to our case, is presented in Fig. 6-17, clearly showing the way a V-defect is formed by a SMB. A detailed description of this defect formation is presented in Chapter 7 (paragraph 7.2.2).

![Fig. 6-17: A model proposed for the V-pits creation, from SMBs formed in the steps sites [136].](image)

A typical example of a HRTEM image showing the AlN/SiC interface is presented in Fig. 6-18, where the arrow shows the presence of a dislocation-like strained area in the 6H-SiC/AlN interface. This area is extensively analysed and discussed in Chapter 7.
Fig. 6-18: A HRTEM image showing a step with a formed defect in the 6H-SiC/AlN interface.

In Fig. 6-19, the strain analysis results obtained for a selected area in the HRTEM image of Fig. 6-18, based on geometric phase algorithms (GPA), is presented. More specifically, the $e_{xx}$ and $e_{yy}$ strain maps are shown (in (a) and (b) respectively), where the arrow indicates the defect existing in the 6H-SiC/AlN interface.

Fig. 6-19: (a) $e_{xx}$ and (b) $e_{yy}$ map of a selected area of the HRTEM image of Fig. 6-18.
6.4.3 Surface of the multilayer structure

After the thick GaN buffer layer growth, the GaN/AlGaN heterostructure is deposited, with an AlN spacer layer grown in between. By magnifying the upper part of the structure of TEM image of Fig. 6-11, the free surface of the specimen is clearly seen. In the HRTEM images of Fig. 6-20, the surface of this sample is revealed, where the presence of glue indicates the end of the sample. More specifically, the surface is almost sharp with no undulations (unlike the on axis case).

![HRTEM image showing the AlN spacer layer](image)

**Fig. 6-20:** A HRTEM image of the top layers of this structure, showing the AlGaN/GaN heterostructure.

The AlN spacer layer is distinguished between the GaN and the AlGaN layers, whereas the AlGaN/GaN cap interface is not clearly visible. The HRTEM image of Fig. 6-21 reveals better the characteristics of the AlN spacer layer. This layer does feature an almost uniform thickness and clear interfaces with the AlGaN and GaN layers (the white arrows indicate the thickness of the AlN layer).

![HRTEM image showing the AlN spacer layer with thickness indication](image)

**Fig. 6-21:** A HRTEM image showing the AlN spacer layer—the arrows indicate the thickness of this layer.
Furthermore, the in order to indicate the GaN cap layer grown on the top of the AlGaN barrier layer (as shown in the HRTEM image of Fig. 6-22), FFT was performed and is presented in Fig. 6-22 (b). After magnifying a specific part of the FFT (presented as inset), the double spots noted with no1 and 2 are revealed, indicating the presence of materials with slightly different lattice parameters. Indeed, the reconstruction of the lattice fringes via a filtered IFFT using only the indicated by no1 and 2 spots represents the areas that give rise to these spots, as shown in Fig. 6-22 (c) and (d) respectively. According to the theoretical values for the lattice constants for AlGaN (~20% Al) and GaN layers (5.072 and 5.189 respectively), the lattice constant ratio towards c-axis, is 1.023. Taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.019, close enough to the theoretically obtained ratio. Thus, the IFFT results of Fig. 6-22 (c) indicate the AlGaN material (obtained from spot no1) and the IFFT results of Fig. 6-22 (d) the GaN material (obtained from spot no2), grown on top of the AlGaN layer.

![Figure 6-22](image)

**Fig. 6-22:** (a) A HRTEM image showing the surface of the structure, (b) the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots. (c) IFFT using only the spot noted with no1 that corresponds to AlGaN. (d) IFFT using only the spot noted with no2 that refer to GaN-cap layer.
6.5 TEM results-Sample #TG2135 (2 deg off)

In Table 6-8, the nominal and experimental thicknesses of the multilayer structure grown on 2 deg off 4H-SiC substrate are presented:

<table>
<thead>
<tr>
<th>Layers numbering</th>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
<th>Experimental thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlN nucleation layer</td>
<td>60-90</td>
<td>11.3-38</td>
</tr>
<tr>
<td>2</td>
<td>GaN buffer</td>
<td>1720</td>
<td>1580-1600*</td>
</tr>
<tr>
<td>3</td>
<td>GaN undoped channel</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>AlN spacer</td>
<td>1</td>
<td>3-5</td>
</tr>
<tr>
<td>5</td>
<td>AlGaN (~20%Al)</td>
<td>20</td>
<td>19-21**</td>
</tr>
<tr>
<td>6</td>
<td>GaN cap</td>
<td>2-2.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 6-8: Nominal and experimental thicknesses of Sample #TG2135

*It refers to the overall thickness of layers 1 and 2 **It refers to the overall thickness of layers 5 and 6.

Similarly to the previous samples, a typical electron diffraction of Fig. 6-23 taken from a selected part containing part of the substrate/film interface area (along [11\(\overline{2}\)0] SiC), confirms the very good epitaxial growth of the epilayers on the 4H-SiC substrate.

![Fig. 6-23: A typical electron diffraction pattern obtained from a selected area containing part of the 4H-SiC substrate and the first grown layers along [11\(\overline{2}\)0] SiC. The very good epitaxial growth of GaN layers on the 4H-SiC substrate is clear.](image)

It is clear for the epitaxial relationships that the [0001] SiC direction is parallel to the [0001] GaN direction, the [\(\overline{1}\)100] SiC direction is parallel to [\(\overline{1}\)100] GaN direction and the [11\(\overline{2}\)0] SiC direction is parallel to [11\(\overline{2}\)0] GaN direction. The main spots of the two phases are indicated with arrows, pointing to the right for GaN and to the left for SiC.
Moreover, a typical electron diffraction pattern of Fig. 6-24 (taken from a selected area containing part of the nitride layers (AlN/GaN/AlGaN)), taken along [11̅00], reveals the very good epitaxial growth of GaN on the AlN layer. Similar to this are also the patterns at the other interfaces. The main spots of the two phases are indicated with arrows. Moreover, in the magnified part of the electron diffraction pattern presented as inset in Fig. 6-24, the presence of a third spot is highlighted placed in between the spots corresponding to AlN and GaN elements. This spot probably corresponds to the AlGaN layer, with lattice constants values in between the ones of AlN and GaN.

![Fig. 6-24: A typical electron diffraction pattern taken from a selected part, containing part of the AlN/GaN/AlGaN layers, along [11̅00] AlN and GaN, revealing the very good epitaxial growth of GaN on the AlN layer.](image)

For the structural characterization of the epilayers and interfaces cross-sectional TEM analysis was carried out. The conventional bright field image of Fig. 6-25 shows the multilayer structure grown on the 2 deg off 4H-SiC. In the upper part of the structure, the glue used for the preparation of the samples, clearly indicates the end of the sample.
Fig. 6-25: A low magnification TEM images showing the multilayer structure grown on (0001) 4H-Si substrate. Contrast changes reveal layers sequence grown epitaxially on the substrate.

As clearly presented in Fig. 6-25, defects-mostly dislocations are observed, that begin from the AlN/GaN interface and expand towards the surface of the structure. However, the dislocation density though is much smaller (~3.5 \( \cdot \) 10^9 cm\(^{-2}\)) as compared to the on axis sample case. As we move towards the structure surface, dislocations sharply decrease, with only a few of them reaching the top layers. This fact is very important indicating a higher crystal quality GaN epilayers and thus a higher quality heterojunction and 2DEG channel performance [110].

Closed dislocation loops are observed in this case too, with a characteristic loop pointed by a white arrow in Fig. 6-25. A significant fraction of TDs bend into the basal plane and by reacting with dislocations of the opposite phase, they are eliminated by forming closed loops in the lower regions of the GaN epilayer [116].

In the next TEM images, magnified parts of the multilayer structure are shown (from bottom to top).
6.5.1 The effect of the AlN nucleation layer

Cross-sectional TEM analysis was carried out in order to study the structure of the AlN nucleation layer. The TEM image of Fig. 6-26 shows the first grown AlN nucleation layer, which presents a thickness not exceeding 40nm. Although it is too thin to accommodate the stress induced due to TEC mismatch, no cracks are observed in the epilayers.

![Fig. 6-26: A TEM image revealing the structure of the AlN nucleation layer.](image)

Similarly to the previous cases, as observed in Fig. 6-26, the AlN nucleation layer is composed of a high density partially coalesced V-shapes with random shapes. The sides of the pits appear to be aligned with specific crystallographic directions. The V-structures mostly present an angle of about 60°, with [1011] sidewalls. V- widths of 20-45 nm are observed and their depth is 20-25 nm. A magnified V-structure is shown in Fig. 6-27.

![Fig. 6-27: A low magnification TEM image showing an individual V-defect.](image)

A characteristic HRTEM image shows the GaN/AlN nucleation layer area, as presented in Fig. 6-28. A Fast Fourier Transform (FFT) performed in the area indicated by the white rectangular is presented at Fig. 6-28 (a). A specific part of the FFT is magnified and presented as inset, revealing the existence of double spots and thus the presence of materials with slightly different lattice constants. According to the theoretical values for the lattice constants for AlN and GaN layers (4.997 and 5.189 respectively), the lattice constant ratio towards c-axis, is 1.038. In this case, taking into account the FFT results, the distance of each one of the double spots gives for the c-axis a ratio equal to 1.042, which is close enough to the
theoretically obtained ratio. This fact indicates the presence of GaN into the V-structures formed in the AlN nucleation layer.

Fig. 6-28: (a) A HRTEM image showing a V-structure, (b) the resulting FFT. An enlarged part shown as inset makes clear the splitting of the diffracted spots.

6.5.2 Steps in the 4H-SiC/AlN interface

Fig. 6-29 shows a typical HRTEM micrograph of the AlN nucleation layer/4H-SiC interface for this sample (2 deg cut-off). As clearly revealed, the surface of the 4H-SiC substrate consists of (0001) atomically flat and smooth terraces and one atomic layer steps (0.25nm height). White arrows in Fig. 6-29 indicate the parallel and periodic over the substrate surface steps positions. Moreover, the steps are perpendicular to [1120] direction (or aligned along [1100] direction) and the distance between the steps (length of terraces) of about 6 nm is found to correspond to the 2 degrees off-cut. In this case (#TG1929), since the step density is high and so the terraces are not too long, incorporation of aluminum (Al) and nitrogen (N) atoms takes place at the step edges during growth, whereas growth on the terraces is limited. Thus, step flow growth is induced initiating from the steps positions, with direction determined by step orientation [137].

Fig. 6-29: A HRTEM image indicating the steps in the 4H-SiC/AlN nucleation layer interface.

Furthermore, in 2 deg off-cut substrates, the growth on the steps positions, inherits the stacking order of atoms from the substrate. However, the step height is determined not by the
AlN epilayer, but by the 4H-SiC substrate, and also the step height of 4H-SiC is not equal to the unit-cell of AlN. More specifically, the bilayer distance along c-axis for 4H-SiC is ~2.51Å and for AlN ~2.49Å. Thus, a number of defects are created in the steps’ positions, as observed in the TEM image of Fig. 6-29. These defects are formed due to the stacking sequence mismatch between the two sides of the step, left and right of it and are discussed in Chapter 7 (in paragraph 7.2.2).

The V-defects formation mechanism strongly depends on the different growth rate laterally and vertically, with a higher vertical growth rate as compared to the lateral-sidewalls growth. More specifically, a reduced Al incorporation (and thus growth rate) on the reversed pyramid walls ([1011]) in comparison with the (0001) planes probably resulted in this defect formation [119]. Thus, the steps existing in the 4H-SiC/AlN interface enhance the V-pit formation, at the positions where different AlN domains meet each other, combined with the slow growth (1011) facets [125]. In other studies ([120]–[122]), it was reported that threading dislocations can initiate the V-defect.

### 6.5.3 Surface of the multilayer structure

Fig. 6-30 presents the upper part of the structure, where the heterostructure layers area is revealed. As shown in this image, after the thick GaN buffer layer growth, the GaN/AlGaN heterostructure is deposited, with an AlN spacer layer grown in between. Again, similarly to the 1 deg off axis case, unlike the on-axis situation, a sharp and undulation free structure surface is reported. However, in this case, stacking faults are formed due to the misfit strain, as clearly observed in the HRTEM image of Fig. 6-30 [129].

![Fig. 6-30: A TEM image showing the upper layers of the structure grown on 4H-SiC (2 deg off) substrate.](image)
The low Al concentration (21%, less than 25%), in combination with the fact that the AlGaN layer thickness (19-21nm) does not exceed the critical thickness, results in smooth AlGaN surface in this case [129]. Thus, no strain relaxation situation exists in forms of V-shapes creation, and a maximal electron density should be obtained in the electron channel (2DEG).

Furthermore, the HRTEM image of Fig. 6-31 indicates the growth of the AlN spacer layer featuring an almost uniform thickness and clear interfaces with the AlGaN and GaN layers (the white arrows indicate the thickness of the AlN layer). This fact is very important for the electrical characteristics of the 2DEG channel, which are enhanced with the achievement of abrupt interfaces (decreasing interface roughness scattering effects) [138].

![Fig. 6-31: A HRTEM image showing the AlN spacer layer in between the AlGaN/GaN heterostructure.](image-url)
6.6 Comparison of TEM results

The layers sequence in all samples was the same, exhibiting differences in thicknesses. Table 6-9 presents the layers thicknesses for all presented samples.

<table>
<thead>
<tr>
<th>Layers (bottom to top)</th>
<th>Nominal thickness (nm)</th>
<th>Experimental thickness (nm)</th>
<th>Experimental thickness (nm)</th>
<th>Experimental thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN nucleation layer</td>
<td>60-90</td>
<td>14-35</td>
<td>13-33</td>
<td>11.3-38</td>
</tr>
<tr>
<td>GaN buffer</td>
<td>1720</td>
<td>1827-1849</td>
<td>1680-1700</td>
<td>1580-1600</td>
</tr>
<tr>
<td>GaN undoped channel</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlN spacer</td>
<td>1</td>
<td>1.3-3.5</td>
<td>2-4</td>
<td>2.8-5</td>
</tr>
<tr>
<td>AlGaN (~20%Al)</td>
<td>20</td>
<td>22.3-30.8</td>
<td>20-21</td>
<td>19-21</td>
</tr>
<tr>
<td>GaN cap</td>
<td>2-2.5</td>
<td>4H-SiC (±0.5 deg off)</td>
<td>6H-SiC (1 deg off)</td>
<td>4H-SiC (2 deg off)</td>
</tr>
</tbody>
</table>

Table 6-9: Nominal and measured thicknesses for structures grown on almost on axis, 1 deg off and 2 deg off SiC substrates.

Comparing the two samples grown on 4H-SiC using MOVPE method:

First of all, in most of the layers the thickness decreases, as the misorientation angle increases. This fact can easily be explained by a potential growth rate difference (as in the work of Rudzinski et al. [137]) grown in the same growth run.

Steps perpendicular to [1120] direction (or aligned along [1100] direction) were observed in the 4H-SiC/AlN nucleation layer interface in #TG2135 sample (forming no step-bunching), corresponding to the 2 deg off angle. Moreover, characteristic contrast in the TEM images suggested the growth of defects in the AlN layer that begin from the 4H-SiC/AlN interface at the steps’ positions, due to stacking mismatch difference between the AlN domains grown at the two sides of the step.

In the 2 deg off axis case, since the step density is high with not too long terraces (6nm), incorporation of aluminum (Al) and nitrogen (N) atoms takes place at the step edges during growth, whereas growth on the terraces is limited. Thus, step flow growth is induced initiating from the steps positions, with direction determined by step orientation [137]. On the other hand, as the misorientation angle decreases, the terrace width increases. Indeed, in #TG1929 sample, random and less dense steps were observed in the 4H-SiC/AlN interface, due to the almost on-axis substrate (± 0.5 deg off). Thus, with an almost zero the steps density, and with a greater terraces length, epitaxial growth initiates on terraces (because the terraces length is greater compared with the migration length of atoms) on the surface randomly and the growth direction is not determined by the step orientation as in the off axis sample case. Moreover, even with an almost zero off cut, a small number of steps still exists, resulting to defect
formation. Finally, defects are also formed beginning from the SiC/AlN interface due to the orientation mismatch at the grain boundaries between the different AlN grains, formed during growth on the substrate surface.

In both cases, the AlN nucleation layer is full of structural defects and features not completely-partially coalesced V-shaped defects with random shapes. They present an angle of about 60°, with [10\(\bar{1}\)1] sidewalls. However, these defects are flat-topped, better defined and of smaller size in the on-axis sample. Obviously, an increase of the AlN thickness (from 35 nm for on axis sample to 38 nm for off axis sample) results in a small increase of the V-defect size. Moreover, due to thickness increase and 2 deg cut-off, the defects density is higher in the off axis sample case.

Furthermore, dislocations appear in the down GaN layer starting from the AlN/GaN interface in all samples. The dislocations’ density is greater in the on axis sample case, probably due to strain relaxation reasons [134], [135]. Generally, the strain relaxation mechanisms involved in each sample are dependent on the substrate miscut angle [139]. According to J. Pernot et al. [139], in the on axis case, during AlN nucleation layer growth, the coalescence of misoriented islands could have resulted in threading dislocations formation, relaxing the strain. On the other hand, during AlN nucleation layer growth in the off axis case, the island formation is limited and thus the isolated threading dislocation density is also limited. In this case, a step flow growth is favored, and other relaxation mechanisms appear (in forms of various types of dislocations and stacking faults formation) [139].

The AlN/SiC interface is characterized by a high initial TD density followed by a gradual reduction in the GaN layer (at the distance <600 nm from the substrate) in density as the film continues to grow. Closed dislocation loops are observed in both cases, being more intense in the on axis sample case. Generally, TDs bend into the basal plane and react with dislocations of the opposite phase, and are eliminated by forming closed loops in the AlN nucleation layer and in the lower regions of the GaN epilayer [116]. Therefore, the dislocations do not propagate to the upper part of the GaN epilayer, indicating a higher crystal quality GaN epilayer.

In both samples, the AlN spacer layer does not feature a uniform thickness and clear interfaces with the AlGaN and GaN layers, probably having a negative impact in the 2DEG channel electrical characteristics.

Finally, in the on-axis case, the free surface of the specimen appears a characteristic undulation (in forms of V-defects formation), indicating relaxation reasons, whereas in the other sample there is not such situation. This undulation is attributed to the Al\(_x\)Ga\(_{1-x}\)N thickness in combination with the strain via the Al content of the Al\(_x\)Ga\(_{1-x}\)N layer, resulting to relaxation and stress reduction. However, this will then negatively affect the 2DEG densities and sheet resistance.

Similarly to the structural characteristics of the multilayer structures grown on 4H-SiC substrate, the sample grown on 1 deg. off cut 6H-SiC, presented the same characteristics with the other two samples. In sum, some steps were observed in the 6H-SiC/AlN interface, as well
as V-shaped defects were observed in the AlN nucleation layer, with the overgrown GaN epilayer grown into these defects. Moreover, dislocations starting from the AlN/GaN interface, as propagating towards the structure surface, exhibit a sharp decrease. Finally, the AlN spacer layer in between the heterostructure does not show a uniform thickness, and the free surface does not show any relaxation situation (is sharp), not affecting in this way the 2DEG density.

The electrical characterization results, in combination with the STEM/EDX analysis that follows, confirm and enhance the already reported TEM results.

### 6.7 Electrical characterization results

The electrical characteristics of the samples grown on 4H-SiC are summarized in the Table 6-10 [114]:

<table>
<thead>
<tr>
<th>Sample/Off-cut (deg)</th>
<th>$n$ ($\times 10^{13}$ cm$^{-2}$) Hall</th>
<th>$m$ (cm$^2$/V·s) Hall</th>
<th>$R$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample #TG1929/on-axis</td>
<td>1.26</td>
<td>1280</td>
<td>365</td>
</tr>
<tr>
<td>Sample #TG2135/2 deg off</td>
<td>1.03</td>
<td>1410</td>
<td>430</td>
</tr>
</tbody>
</table>

**Table 6-10:** Electrical parameters for the AlGaN/GaN samples grown on SiC of two different off-cuts [114].

As clearly observed in the above Table (6-10), the AlGaN/GaN heterostructure grown on the 2 deg off substrate, shows a better electron mobility, as compared to the corresponding grown on the almost on-axis substrate. This can be explained, combined with the TEM results, by the unrelaxed structure surface as well as the smaller density of dislocations reaching the heterostructure.
6.8 STEM-EDS analysis

In this paragraph, HAADF-STEM images are presented and Energy-dispersive X-ray spectroscopy (EDS) technique is used for the stoichiometric analysis of the layers and interfaces. HAADF-STEM images and EDS elemental maps were acquired by using an aberration-corrected ‘cubed’ FEI Titan 60-300 electron microscope operated at 300 kV, equipped with the ChemiSTEM system [140]. The experiments were carried out at Electron Microscopy for Materials Science (EMAT) laboratory in Antwerp.

In HAADF-STEM mode the scattering is Rutherford-like and therefore the intensity of the formed images is proportional to the atomic number $Z^n$ (1.6 < $n$ < 2) [141] of the elements under investigation and scales with the thickness of the sample. Consequently, the higher $Z$ elements will look brighter in the image compared to the lighter ones which will appear darker.

6.8.1 STEM-EDS analysis of entire structure

In Fig. 6-32, a typical HAADF-STEM image shows the entire multilayer structure. The characteristic Z-contrast observed indicates the presence of elements exhibiting different atomic numbers.

![Fig. 6-32: A HAADF-STEM image showing the entire multilayer structure.](image)

Indeed, the EDS analysis color variations presented in Fig. 6-33 show an Al-enriched AlN layer as well as a thick enough GaN layer grown on top. In order to precisely reveal the elemental composition of the first grown and upper layers of the multilayer structure that are either thin enough or not visible at all in this image, a more detailed HAADF-STEM image is
needed, focusing on these specific areas. These areas are EDS analyzed in the next paragraphs.

![Fig. 6-33: STEM-EDS analysis of the entire multilayer structure where an Al-enriched layer is revealed on the SiC substrate.](image)

### 6.8.2 STEM-EDS analysis of the upper layers

In Fig. 6-34, the HAADF-STEM image shows the upper layers of the multilayer structure. The characteristic Z-contrast indicates the presence of a much heavier (with a larger atomic number) element existing in the layer in between the heterostructure.
Fig. 6-34: A HAADF-STEM image showing the upper layers of the multilayer structure. The arrow indicates the line scan direction presented in Fig. 6-36.

Fig. 6-35: STEM-EDS analysis showing the elemental composition of the upper layers of the multilayer structure.

Indeed, the STEM-EDS map acquired (Fig. 6-35) confirms the presence of an Al-enriched layer in between the AlGaN/GaN heterostructure. After performing a line scan, the distribution of the elements is revealed (Fig. 6-36). The white arrow shown at the HAADF-
Chapter 6: Experimental results

STEM image of Fig. 6-34 indicates the direction of the scan. The Ga and Al content are represented by the green and red colored graph respectively. More specifically, at the very beginning of the graph, the Ga and N content is high enough, indicating the presence of a very thin GaN cap layer. As moving towards the SiC substrate, the Al and N content is increased, whereas the Ga content remains almost constant (at higher levels as compared to the Al content), indicating the presence of an AlGaN layer. Afterwards, the Ga, Al and N content remains almost constant, showing small variations, until the next layer. More specifically, a sharp increase of the Al content denotes an Al-enriched layer, with the simultaneous steep reduction of the Ga content. Finally, the Ga content is increased and the Al is eliminated, indicating the presence of a pure GaN layer. Thus, the upper part exact layers sequence is GaN/AlN/AlGaN/GaN.

![Fig. 6-34](image)

The colored areas noted in Fig. 6-37 were selected for the atomic stoichiometry computation %. Table 6-11 presents the computation results. The fraction of Al and N in the AlN interlayer was computed ~40% and ~44% respectively (green region).

![Fig. 6-37](image)

<table>
<thead>
<tr>
<th>REGION</th>
<th>STOICHIOMETRY (ATOMIC %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>Ga:52.74 N:47.26</td>
</tr>
<tr>
<td>Green</td>
<td>Al:39.55 Ga:16.39 N:44.05</td>
</tr>
<tr>
<td>Blue</td>
<td>Al:11.81 Ga:40.07 N:48.12</td>
</tr>
<tr>
<td>Yellow</td>
<td>N:44.68 Ga:55.32</td>
</tr>
</tbody>
</table>

![Table 6-11](image)

Fig. 6-36: Line scan revealing the distribution of the elements. The direction of the scan is indicated by the white arrow at the HAADF-STEM image of Fig. 6-34.

Fig. 6-37: HAADF-STEM image of the upper layers. The colored areas denote the regions used for the computation of the elemental stoichiometry, as presented in Table 6-11.
However, the presence of Ga inside the AlN spacer layer denotes non-sharp AlGaN/AlN/GaN interfaces: a ~16% Ga fraction is computed in the green region presented in Fig. 6-37. Moreover, the Al content into the AlGaN barrier layer is almost 12% (blue region).

It is worth mentioning that even though the AlN spacer layer contains a small but significant Ga quantity (almost 17%), the GaN channel layer does not present any interdiffusion signs. More specifically, it presents a Ga and N quantity of 53% and 47% respectively, with no Al content. Moreover, the presence of the GaN cap layer is clearly observed, on the top of the heterostructure. The Ga content in this layer is ~55%.

### 6.8.3 STEM-EDS analysis of the first grown layers on 6H-SiC

A characteristic V-shaped defect, already observed using CTEM in the first grown AlN nucleation layer grown on the 6H-SiC substrate, is shown in a characteristic STEM-HAADF image in Fig. 6-38. The characteristic contrast of the V-shaped defect clearly indicates the presence of a different stoichiometry element.

![Fig. 6-38: A HAADF-STEM image showing a V-shaped defect.](image)

Moreover, the contrast observed in the 6H-SiC/AlN interface shown in Fig. 6-39, indicates the presence of a one atomic layer element with different composition. The atomic numbers of Al, Ga and N are 13, 31 and 7 respectively. The lighter contrast means that a heavier element (with a greater atomic number) exists in these regions. A STEM-EDS analysis is
needed in order to clarify the situation, as presented below. Furthermore, in Fig. 6-39, a step in the 6H-SiC/AlN interface is clearly seen (its exact position is marked with an arrow).

**Fig. 6-39:** A HAADF-STEM image showing the 6H-SiC/AlN interface. The white arrow is pointing to the step in the interface.

**Fig. 6-40:** A HAADF-STEM image showing the first grown layers of the multilayer structures on a 6H-SiC substrate. The white arrow indicates the direction of the line scan presented in Fig. 6-42.
After selecting the specific region marked with a white colored rectangular in Fig. 6-40, the EDS analysis (Fig. 6-41) shows a Ga presence at the high contrast region between the 6H-SiC substrate and AlN layer, observed at the previous HAADF-STEM image. Moreover, the GaN grown on top of the AlN layer, obviously starts growing inside the V-defects. However, a Ga diffusion is observed in a region near the AlN/GaN interface, as denoted by the green areas into the AlN layer, corresponding to GaN. Finally, the Al element exists in both the AlN layer and the V-defect, but with a slightly smaller concentration. In order to precisely indicate the composition of the elements in the layers, in the following paragraphs, exact computation of the elements content is presented.

**Fig. 6-41:** STEM-EDS analysis showing the elemental composition of the first grown layers of the multilayer structure grown on 6H-SiC.
Furthermore, after performing a line scan, the distribution of the elements is revealed (Fig. 6-42). The white colored arrow at the HAADF-STEM image shown in Fig. 6-40 indicates the direction of the scan.

**Fig. 6-42:** Line scan revealing the distribution of the elements. The white arrow at the HAADF-STEM image of Fig. 6-40 indicates the direction of the scan. It is clear that Ga is present at the high contrast region between the SiC and AlN regions, which is shown at the HAADF-STEM image.

More specifically, the Al, Ga and N distribution are denoted with red, green and blue colored lines in the graph respectively. It is clearly observed that the Al and N concentration is almost constant at the beginning (with a small increase in the Al content) as approaching the 6H-SiC/AlN interface. However, an abrupt reduction right after the interface for both elements is clear. It is worth saying that Al is present in the V-defect as well, probably due to interdiffusion between the layers. Ga distribution in the area across the arrow shows a gradual reduction as scanning towards the substrate. However, a peak is observed exactly in the AlN/6H-SiC interface, indicating the presence of a Ga monolayer. The EDS spectrum acquired from the same region, in Fig. 6-43, reveals the elements that are present (and once again the presence of Ga is undisputable).

**Fig. 6-43:** EDS spectrum acquired from the previous region revealing the elements which are present.
If we select a more specific and smaller region of the HAADF-STEM and perform EDS analysis, the presence of the Ga layer in between the SiC/AlN interface is more obviously observed (Fig. 6-44).

![Fig. 6-44](image)

**Fig. 6-44:** A HAADF-STEM image and the corresponding EDS analysis showing the elemental composition of the 6H-SiC/AlN interface of the multilayer structure.

The line scan across the arrow noted in Fig. 6-45, shows again more intensively the presence of Ga in the interface and the diffusion of Ga in the AlN layer.

![Fig. 6-45](image)

**Fig. 6-45:** Line scan revealing the distribution of the elements. The direction of the scan is indicated by the white arrow at the HAADF-STEM image (Fig. 6-44).
Finally, after selecting specific regions in Fig. 6-46, the exact % stoichiometry is computed and shown in Table 6-12. In particular, in the green colored area the Al content is ~18% and there is a small amount of Ga (1.42%). In the blue colored area, the Al concentration is ~ 58% and there is also a small percentage of Ga (0.64%). This fact clearly denotes an interdiffusion situation. As we move towards the V-defect, in the yellow colored area, the Al and Ga content was computed ~46% and ~13% respectively, once again showing presence of Al in the V-defect (by forming AlGaN areas).

![Fig. 6-46: A HAADF-STEM image of the first grown layers. The colored areas denote the areas used for the computation of the elemental stoichiometry, as presented in Table 6-12.](image)

<table>
<thead>
<tr>
<th>REGION</th>
<th>STOICHIOMETRY (ATOMIC %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>Si:55 C:45</td>
</tr>
<tr>
<td>Green</td>
<td>Si:34.53 Al:17.98 C:29.14 N:16.93 Ga:1.42</td>
</tr>
<tr>
<td>Blue</td>
<td>Al:57.91 N:41.45 Ga:0.64</td>
</tr>
<tr>
<td>Yellow</td>
<td>Al:46.45 N:40.59 Ga:12.98</td>
</tr>
</tbody>
</table>

**Table 6-12:** Elemental stoichiometry in the layers.
6.8.4 STEM-EDS analysis of the first grown layers on 4H-SiC

The HAADF-STEM image of Fig. 6-47 presents the AlN/GaN layers area grown onto a 4H-SiC substrate. Similarly to the previous case (grown onto a 6H-SiC substrate), the Z-contrast existing in the AlN/SiC interface in the HAADF-STEM image clearly denotes the presence of a greater atomic number element, which, based on the EDS analysis results (Fig. 6-48 to 6-50) is proved to be Ga.

![Image](image_url)

**Fig. 6-47:** A HAADF-STEM image showing the first grown layers of the multilayer structures on a 4H-SiC substrate. The white arrow indicates the direction of the line scan of Fig. 6-50.

As clearly illustrated in the line scan of Fig. 6-49 (with direction indicated by the arrow shown in Fig. 6-47), a Ga presence is also observed into the AlN layer (small enough, but detectable), indicating an interdiffusion situation. Moreover, as indicated by the EDS analysis of Fig 6-48, the V-shaped defect walls are constituted by AlGaN areas, with decreasing Al content as moving inside the V and towards the structure surface. The EDS spectrum of Fig. 6-50 clearly states the Ga presence at the AlN/SiC interface.
Fig. 6-48: STEM-EDS analysis showing the elemental composition of the first layers of the multilayer structure grown on 4H-SiC.

Fig. 6-49: Line scan revealing the distribution of the elements. The white arrow at the HAADF-STEM image of Fig. 6-47 indicates the direction of the scan.
Fig. 6-50: EDS spectrum acquired from the region scanned and shown in Fig. 6-49, revealing the elements which are present.

Comparing the Ga layer thickness existing in between the AlN/SiC substrate interface, it is clearly observed in the magnified parts of the previously reported line scans, as presented in Fig. 6-51, that the Ga layer thickness is greater in the 4H-SiC as compared to the 6H-SiC case. As noted in Fig. 6-51, the thickness of this Ga layer is around 0.5 nm (corresponding to the GaN unit-cell) in the 4H-SiC/AlN interface and around 0.25 nm in the 6H-SiC/AlN interface (corresponding to almost the half of GaN unit-cell).

Fig. 6-51: Line scan revealing the distribution of the elements in the (a) 4H-SiC/AlN and (b) 6H-SiC/AlN interfaces. The direction of the scan is heading towards the SiC substrate.
However, there are some individual areas, where exactly one Ga monolayer is found in the AlN/4H-SiC interface, as shown in Fig. 6-52. The arrows point to the steps existing in the interface.

Fig. 6-52: A HAADF-STEM image showing the first grown layers of the multilayer structures on a 4H-SiC substrate.

### 6.8.5 2D-GaN formation-Interpretation-Properties

The presence of the Ga in the SiC/AlN interface could be explained as follows:

During the CVD procedure of growth run, at the beginning, the baking of the reactor and graphite susceptor in hydrogen at >1100°C takes place. The aim is the decomposition of all nitrides from previous growth runs and also the cleaning of the susceptor. In this way, all Ga-containing deposit is evaporated and removed from the chamber but not from the reactor inlet of gas mixture because this part of chamber is rather cold. Thereafter, SiC sample is loaded and being seated in a wafer pocket on susceptor (graphite coated with CVD-SiC). The SiC sample annealing in H₂ using T>1100°C at low pressure follows in order to clean Si-surface of the hexagonal SiC. After that, the temperature is reduced to ~1000°C at ~100mbar absolute pressure and ammonia is introduced into the reactor. Thus, surface gets nitridated but for a short time ~30-60s. Finally, the introduction of Aluminum precursor (TMAI) takes place and growth starts. Ammonia is kept flowing during all growth until the very end.

Since the inlet of reactor is usually contaminated with enough Ga-precursor (TMGa and it's adducts) the possibility of Gallium deposition during growth in MOCVD cannot be excluded. However, the interesting thing is that a single monolayer of Ga exists in the AlN/SiC interface. It may be energetically favored to keep Ga bounded to SiC surface. Right after the Al-precursor introduction, there is a so high Al supply, that pure AlN is grown even if Ga source remains active.
Regarding the as called "memory effect" in MOCVD, described in literature [142], [143], it is very much different from this case. Memory effect refers to abrupt change in gas-phase composition during growth, i.e. when growing GaN:Mg (Mg-doped, with Ga/Mg ratio usually <1000) followed by undoped GaN (without intentional doping, Mg-is off). There is some Mg accumulated on sample surface and its concentration decay is easily measurable in the nominally "undoped" part of GaN structure. Therefore, this SiC/Ga/AlN interface is something different and has not been previously reported and it is not what is commonly described as "memory effect" in MOCVD (although being a sort of memory though).

The Ga monolayer presence in the AlN/SiC interface could be related to a sort of memory effect. Moreover, we cannot exclude the probability of Ga interdiffusion through the defects-SMBs formed in the steps positions inside the AlN layer. In either case, a 2D GaN monolayer is formed in the AlN/SiC interface, probably offering great opportunities for nanoelectronic devices [144].

It is recently reported that 2D nitrides are key to advancing novel devices, with the layered hexagonal boron nitride (hBN) being already tested. Moreover, wurtzite GaN is predicted to reconstruct into a 2D hexagonal graphitic structure when thinned to few atomic layers, resulting to thickness-dependent energy bandgap ($E_g$) via quantum confinement. It has already been reported that a 2D GaN is grown via a novel migration-enhanced encapsulated growth (MEEG) technique utilizing epitaxial graphene, with the graphene playing a critical role in stabilizing the direct bandgap, 2D buckled structure [144]. According to Z. Balushi et al. [144], the stability of cleaved wurtzite surfaces is affected by surface passivation. When unsaturated states are properly passivated (using partially charged pseudohydrogen), the structure is most stable in the buckled form (as shown in Fig. 6-53 (a)). Either wise, the planar form occurs.

![Fig. 6-53: Properties of 2D nitrides from ab initio hybrid density functional theory. (a) Binding energy calculations of freestanding planar and buckled 2D nitrides (M: group-III metal element, N: nitrogen and H: hydrogen atoms), as a function of layer number (L), showing increased stability of the buckled structure resulting from their decreasing binding energies relative to planar 2D nitrides. (b) Band-structure calculations via DFT meta-GGA of freestanding planar and buckled 2D monolayer GaN, illustrating buckled 2D GaN with a direct bandgap ($E_g$) of 5.28 eV and planar 2D GaN with indirect $E_g$ of 4.12 eV, both larger than the direct $E_g$ of wurtzite bulk GaN (3.42 eV) due to quantum confinement. (c) Diagram of bandgap energy versus in-plane lattice parameter for bulk and buckled 2D nitrides, establishing the possibility of probing deep into the ultraviolet with monolayers of group-III nitrides. The $E_g$ as a function of number of atomic buckled layers is included as an inset in (c) [144].]
In Fig 6-53 (a), the binding energy of the 2D planar and buckled structures as a function of layer number is presented. More specifically, the freestanding buckled structure exhibits a more negative binding energy when compared to the planar structure, and so it is considered the preferred configuration for 2D nitrides, regardless of the number of layers. In Fig 6-53 (b), the direct bandgap of buckled structure is clearly observed (in contrary with the indirect of planar structure). Thus, the most stable structure is the buckled one, indicating that 2D nitrides (and alloys) are viable candidates for tunable optoelectronics (Fig. 6-53 (c)).

A schematic of the proposed MEEG process [144] is shown in Fig. 6-54. The starting substrate consists of epitaxial graphene formed by sublimation of Si from the SiC surface (0001) (Fig. 6-54 (a)), which is converted to quasi-freestanding epitaxial graphene (QFEG) via hydrogenation. Hydrogenation passivates dangling bonds between graphene-buffer/SiC (0001), converting the graphene-buffer to an additional layer of graphene and thus creating a pristine interface of reduced energy for the realization of 2D nitrides via MEEG. QFEG/Si (0001) is then exposed to cycles of trimethylgallium at 550°C (Fig. 6-54 (c)), which decomposes to gallium adatoms that diffuse readily on the surface of graphene, subsequently intercalating between QFEG/SiC (0001). Finally, transformation of the intercalated gallium to 2D GaN is performed via ammonolysis at 675°C. During this process, atomic nitrogen resulting from the decomposition of ammonia, intercalates graphene and reacts with gallium to form 2D GaN.

Fig. 6-54: Schematic of the proposed migration-enhanced encapsulated growth (MEEG) process.
Chapter 7: Quantitative analysis

Interfaces at multilayer structures grown on SiC

7.1 Principles of study

In general, HRTEM micrographs consist of periodically arranged dots depicting the periodicity of the crystal’s potential projection. This is consistent with the electron diffraction (ED) patterns periodicity that visualizes the Fourier Transform of the function presenting the crystal potential. In this perspective, every diffracted spot (beam) corresponds to a spatial frequency and consequently to a simple linear grating. These arguments stand for every individual direction on the HRTEM micrographs and ED patterns and the superposition of all gratings could represent the final image.

Therefore the main (spatial) frequency controls the main periodicity on the HRTEM image along any specific direction. All the other diffracted beams correspond to higher order spatial frequencies of the Fourier Transform and modulate in some way the intensity of the dots in the final image. Thus, the intensity distribution in any direction on a HRTEM micrograph represents precisely the periodicity of the image, especially in the case of non-modulated structures. This fact applies for both bright and dark dots that compose the image.

According to the previous statements, the main characteristics of the intensity distribution could be illustrated performing a simple fitting with a sinusoidal function of the form:

\[ y(x) = y_0 + A \cdot \sin \left( \pi \cdot \frac{x-x_c}{w} \right) \]  \hspace{1cm} (7-1)

where A is the amplitude (the peak deviation of the function from zero), w is the periodicity and x_c the phase of the wave.

In order to testify the above statements, we applied the fitting process to the intensity profiles obtained from several types of images (experimental, averaged and simulated images). More specifically, Fig. 7-1, 7-2 and 7-3 show an example of this analysis applied on an experimental, averaged and simulated image respectively, with the averaged and simulated ones being superimposed on the corresponding part of the experimental micrograph. After performing a line scan across the line indicated by the arrow in each one of the different types of images, the resulted intensity distribution (noted with a dashed line) is shown in Fig. 7-1 (b), 7-2 (b) and 7-3 (b) for the experimental, averaged and simulated image respectively. After that, using equation (1), a sine fitting was performed in the obtained intensity profiles, and the resulted graph (noted with a continuous line) is presented in Fig. 7-1 (b), 7-2 (b) and 7-3 (b) for the experimental, averaged and simulated images respectively.
Fig. 7-1: (a) A HRTEM experimental image presenting the 6H-SiC structure, (b) The fitting of the intensity distribution along the dots’ line shown by the white arrow on the micrograph, using a simple sine function.

Fig. 7-2: (a) An averaged image presenting the 6H-SiC structure, superimposed over the HRTEM image, (b) The fitting of the intensity distribution along the dots’ line shown by the white arrow on the micrograph, using a simple sine function.

As clearly observed, in all cases the very good fitting is obvious as also confirmed by the resulted adjusted $R^2$ value. More specifically, in the experimental image case (Fig. 7-1 (a)), the very good fitting is presented in Fig. 7-1 (b) (noted with red color-continuous line), with an adjusted $R^2$ value equal to 0.75134. Furthermore, in the averaged image case (Fig. 7-2 (a)), the excellent fitting is presented in Fig. 7-2 (b) (noted with red color-continuous line), with an adjusted $R^2$ value equal to 0.99477. Finally, the excellent fitting results were also confirmed in the simulated image case as well (Fig. 7-3 (a)), where the intensity profile fitting method was performed not only for the white, but also for the black dots in the image, with an adjusted $R^2$ value around 0.85 for both cases. The intensity profile of the black and white dots is represented by the red and black dashed line graphs respectively with the fitting results represented by the same color continuous line graphs (Fig. 7-3 (b)). Thus, the results obtained for the three kinds of images show that this simple analysis stands very well in every case.
Fig. 7-3: (a) A simulated image presenting the 6H-SiC structure, superimposed over the HRTEM image (b) The fitting of the intensity distribution along the white dots’ line shown by the white arrow (red colored graph) on the micrograph and along the black dots line underneath (black colored graph), using a simple sine function.

To sum up, by applying this simple sine fitting in any direction in a HRTEM micrograph, many useful quantitative results can be obtained, important for the building of models and simulations. More specifically, the periodicity (\( w \)) extracted from the sine fitting results, denotes the spots periodicity in the HRTEM image in the specific direction, and thus the lattice constants of the elements and any strain existing along \([11\overline{2}0]\) as well as along \([0001]\) c-axis. Furthermore, the phase (\( \chi_\phi \)) of the sine function, represents the wave propagation characteristics. Thus, by comparing the phase (\( \chi_\phi \)) for successive rows of dots, the shifting between them can easily reveal the sequence of the stacking and also any disturbance existing. Finally, it is possible to perform the fitting over the whole intensity distribution or over discrete parts of it, in order to highlight better the differences that exist among the several parts of the image.

### 7.1.1 Nitride binding configurations to SiC

According to many years of studies in the growth of III-V alloys on SiC substrate (both 4H-SiC and 6H-SiC), the substrate plays a very important role in the quality of the deposited materials. The lattice mismatch and strain induced is a parameter affecting this quality. Moreover, due to the fact that the AlN and GaN materials are partly ionic and partly covalent, another factor plays also an important role: the interfacial polarity. As mentioned, the materials exhibit electric fields because of the heterovalent interface character and also the piezoelectric characteristics.

More specifically, Capaz et al. [145] suggested that the interface polarity matching determines the lower-energy systems, showing strong binding for Si-N and C-Ga interfaces and weak for Si-Ga and C-N interfaces for GaN growth on (0001) 6H-SiC substrate. Other studies [146] have proved that a large positive interfacial charge is observed on a Si-terminated SiC substrate, attracting nitrogen (N) and resulting in a better epitaxial growth and quality of the GaN or AlN epilayers. Moreover, Städele et al. [147] have reported that the
preferable 3C-SiC/AlN or GaN interface bonding configurations are Si–N and Ga–C and also that the single mixed layer interfaces are the most stable ones.

M. Sznajder et al. [148] studied the early stages of nitride growth process on silicon carbide. In Fig. 7-4, the possible adsorption sites of the GaN or AlN early stage of growth are indicated in a 1x1 lateral unit cell: the position on-top of the silicon atoms (in case of Si-terminated SiC) of the topmost surface layer, the H₃ or T₄ or in the bridge between two neighbouring topmost atoms. The adsorption of Ga, Al and N atoms are studied on both surface terminations. The adsorption energy is the smallest for the small concentration of adsorbates, for both Si- and C-terminated 4H-SiC surfaces.

**Fig. 7-4:** Structural model showing the possible adsorption sites in a 1x1 lateral unit cell (with the yellow colored circles the Si atoms are represented in the case of Si-terminated SiC and the C atoms in the case of C-terminated SiC).

![Structural model showing the possible adsorption sites in a 1x1 lateral unit cell](image)

The results of this study are presented in Fig 7-5, plotting the adsorption energy $E_{\text{ad}}$ versus Al and Ga coverage. It is obvious that aluminium (Al) binds stronger to the SiC surface than gallium (Ga) at both Si- and C-terminated SiC substrates and for all coverages. For Al, the adsorption on the C-terminated SiC surface is more favorable than on the Si-terminated, exhibiting around 1eV difference. In the case of gallium, this difference is smaller and it equals to maximally 0.4eV at the coverage 1 ML (monolayer). This study proved that at the coverage 1 ML aluminium atoms, on both surface terminations, adsorption on the top of the topmost surface atoms forms a stable monolayer with the adsorption energy of -4.75 eV/atom at SiC (0001) surface and -5.4 eV/atom at the SiC [1100] one. On the other hand, gallium atoms adsorb on the top of the topmost surface atoms only at the SiC (0001) surface with the adsorption energy -4.34 eV/atom. In the case of SiC (0001) surface, the adsorption takes place at the site slightly shifted from T₄ towards the H₃ site and the adsorption energy equals to -
3.97 eV/atom. As a result, both metals are uniformly spread over the 4H-SiC \{0001\} surfaces forming a stable, flat monolayer \[148\].

Furthermore, using a tight binding model, Ren and Dow \[149\] concluded that GaN grown on a C-terminated and Si-terminated SiC substrate shows a local mismatch of 6% and <3% respectively. Moreover, in the study of Stirman et al. \[150\], the GaN/SiC interface is most likely consisting the N-Si bonding arrangement. However, a number of Ga-C bonding is important to be present in the interface by replacing the Si atoms with Ga, as shown in the following Fig. 7-6. More specifically, due to valence mismatch, some intermixing at the interface is essential in order to avoid charge accumulation \[1\].

![Fig. 7-6: (a) Ideal SiC/GaN interface. (b) Rearrangements in the interface using intermixing by replacing the N atom with a C atom for charge balance maintenance \[1\].](image)

### 7.1.2 Computational models for electron-matter interaction-Multislice algorithm

Two basic models are widely used for the simulation of the interaction of an electron beam with matter: the Bloch wave method and the multislice method. In this thesis, the multislice iteration algorithm will be used in order to compute and export the HREM maps corresponding to the structure containing the steps configuration in the AlN/SiC interface. So, it is essential to discuss about some basic information concerning this iteration process.

The multislice algorithm is used in the simulation of high-resolution Transmission electron microscopy micrographs, serving as a useful tool for analyzing experimental images. The basic multislice approach used in most of the simulation packages (e.g. JEMS) is to slice the specimen into many slices normal to the incident beam, which enters the specimen, propagates through it and finally exits it. The specimen is divided into many slices, each of which is thin enough to be approximated as a simple phase shift of the electron beam.

More specifically, as shown in Fig. 7-7, the multislice process goes as follows: First of all, each slice is projected onto a plane somewhere in the slice (usually top, bottom, or middle) giving a projected potential for that slice, the phase grating. After the first interaction of the incident beam with the 1st projection plane, calculations of the amplitudes and phases for all the generated beams are done (many-beam image calculation for a single slice). Furthermore,
the propagation of all those beams until the next phase grating and the scattering calculations are repeated for all the beams incident on each plane. Each calculation produces a new set of beams, which propagate through free space (microscope) to the next phase grating etc. It is important to mention that scattering by the phase grating does not just produce Bragg beams, but keeps track of the scattering in all directions (sampling all of reciprocal space) [69].

![Fig. 7-7: Schematic illustration of the interaction of the incident beam with the specimen: The propagation of all generated beams takes place until the next phase grating and calculations are repeated for all beams incident on each projection plane [69].](image)

**7.2 Results for 6H-SiC/AlN interface (#TG2134)-unstrained step**

In our study, we considered four parts of the experimental micrograph around the step on the 6H-SiC substrate and measured the intensity distribution along directions parallel and perpendicular to the SiC/film interface. Especially for the [0001] direction, we estimated the intensity taking into account a relatively wide area in order to overcome the shifting of the closed-packed layers. Finally, we performed fittings of the intensity along lines parallel and perpendicular to the SiC/film direction.

**7.2.1 Horizontal analysis results**

Based on previous analysis, in Fig. 7-8, the white colored areas numbered from 1 to 36, indicate the area around the step where the intensity distribution is measured and then fitted using the sine function (7-1).
Fig. 7-8: A HRTEM image including the white colored areas, along which intensity distribution and fitting was performed.

Fig. 7-9 shows a characteristic plot of the phase shift, measured in \( d/3 \) units (where \( d \) is the interatomic distance along the direction parallel to the interface that corresponds to the projection of a close-packing layer), as a function of the layers numbering from an arbitrary position far enough from the interface. The results of the horizontal analysis are summarized in the graph of Fig. 7-9.

More specifically, in this graph, the left and right parts of the image are represented by the red and blue colored graph respectively. It is clearly observed that in both parts of the image (right and left), the lower part of the micrograph (left part on the plot) obviously follows the sequence \( \ldots + + + - - - \ldots \) denoting the stacking sequence for the hexagonal 6H-SiC in Hägg.
notation, while the upper part follows the sequence for the hexagonal AlN \(-\ -\ -\ -\). In this way, the starting position of the AlN epilayer is undoubtedly indicated. The comparison of the stacking sequence obtained from the left part of the image (red colored line on the plot) with the sequence from the right one (blue colored line on the plot) shows a characteristic alteration confining the step height, that in our case is one atomic layer. More specifically, the 6H-SiC sequence is continued until the 23\textsuperscript{th} layer on the left part of the image, whereas on the right part it is continued until the 24\textsuperscript{th} layer.

However, the exact starting position of the AlN is not clear; e.g. the AlN stacking sequence is followed beginning from the 22\textsuperscript{nd} layer in the left part of image and so we cannot be sure whether the AlN epilayer growth begins from the 22\textsuperscript{nd} or 23\textsuperscript{rd} layer. The same dilemma stands for the right part of image (24\textsuperscript{th} or 25\textsuperscript{th} layer). Thus, using the advanced microscopy results obtained by STEM-HAADF and STEM-EDX, the chemical analysis revealed the presence of Ga at the 22\textsuperscript{nd} and 23\textsuperscript{rd} layer for the left and right part of image respectively. In this way, the exact starting position of the GaN/AlN epilayers is clearly indicated, denoting the presence of a one-bilayer step. Moreover, it is important to notice that the Ga monolayer existing in the AlN/SiC interface follows the stacking sequence of the SiC substrate, probably due to the fact that it is energetically favourable for the first atomic layer of the material to be grown on the substrate to continue the stacking sequence of it.
7.2.2 V-shaped structures formation origin

In the STEM-HAADF of Fig. 7-10, the origin of the majority of the V-pits existing in the AlN epilayer, is clearly indicated.

![STEM-HAADF image showing V-pit formed by SMB existing in the stepped AlN/SiC interface.](image)

**Fig. 7-10:** A STEM-HAADF image showing a V-pit formed by a SMB existing in the stepped AlN/SiC interface.

More specifically, in the steps position, differences in the stacking were found to exist on the left as compared to the right part of it, according to the analysis previously discussed. This situation points out the presence of stacking mismatch boundaries (SMB), which practically denote twin planes, formed due to the stepped AlN/SiC interface. A magnified part of Fig. 7-10, presented as inset, noted as “2”, shows a characteristic SMB formed in the step position, expanding towards the structure surface and reaching the V-defect (as shown in the magnified part noted as “1”, presented as inset), being responsible for its formation. Due to the presence of a SMB connected to the V-defect apex, we can easily conclude that this defect is in fact a trench defect [98], [123].

However, not all SMBs end up to V-trenches creation. This fact is clearly illustrated in the HAADF-STEM image of Fig. 7-11, where the two steps positions are indicated with white arrows, and where SMBs are formed. In the step on the right part of the image, the SMB does
result in a V-trench formation. On the other hand, at the other step indicated in this image, the SMB does not end up to a V-defect, found to be connected to a stacking fault (SF). The SF area (along [1100]) is magnified and presented as inset, in the top part of Fig. 7-11 (a). Moreover, a FFT (taken from the area of Fig 7-11 (a)) combined with the IFFT results (which occurred using only the spots noted with open circles in the FFT) are presented in Fig. 7-11 (b), highlighting the SF existence.

Fig. 7-11: (a) A STEM-HAADF image showing a V-pit formed by a SMB, (b) FFT and IFFT results, denoting the presence of a SF.
As clearly seen in Fig. 7-11 (a), the SF corrects the stacking sequence between the two differently stacked parts of the SMB. This fact is illustrated in the upper magnified part, by noting the stacking sequence before and after the step, with the sequence after the step changing in a specific point indicated by a white arrow, and becoming the same with the sequence before the step. Thus, in this way the SF terminates the SMB. Since the stacking fault is a rather low energy defect, the SMB can be terminated by overgrowth of the correctly stacked bilayer, without a significant energy cost [151].

Fig. 7-12: A STEM-HAADF image showing a V-pit formed by a SMB existing in the stepped AlN/SiC interface.

According to B. N. Sverdlov et al. [152], SMBs do not form in every step position of the AlN/SiC interface. Moreover, assuming equal probabilities of forming each possible bilayer step, for 6H-SiC a bilayer step leads to a SMB with 2/3 probability. On the other hand, SMBs will always be created on two (2) and four (4) bilayers steps. Indeed, this fact is clear by the analysis below. Based on the STEM-HAADF image of Fig. 7-12, where a bilayer step is
noted with a white arrow, the stacking sequence before and after the step does not change, indicating no SMB defect formation. This can be easily explained, by the fact that the terminations separating the bilayer step (before AlN growth) are ABCA on the left and ABCAC (the letters denote a double layer-bilayer). The first results to CACA AlN, whereas the second to ACAC AlN. Clearly there is no SMB formation in this case. The same situation stands for growth on 4H-SiC substrates, where at one-bilayer steps positions, the possibility for SMB formation is 1/2.

An atomic-resolution ABF (annular bright field)-STEM image of the AlN/GaN/SiC interface is displayed in Fig. 7-13. The image shows not only the presence of heavy elements like Ga and Si. With this technique it is possible to resolve also light elements and to directly determine the polarity of the AlN film (Al face). The situation already described in Fig. 7-12, where no SMB is formed in this kind of step, is illustrated also in the ABF-STEM image of Fig. 7-13.

As a result of this analysis, it is clear that in the 6H-SiC substrate case, the SMB formation can be avoided if the substrate surface contains 1 unit-cell height steps (6 bilayers). However, this situation could result to the formation of other structural defects.

**Fig. 7-13:** An Atomic-resolution ABF-STEM image of AlN/GaN/SiC interface. The inset shows a magnified part of the interface.
7.2.3 Vertical analysis results

Based on previous analysis, in Fig. 7-14, the white colored areas indicate the areas around the step where the intensity distribution is measured and then fitted using the sine function (7-1).

Fig. 7-14: HRTEM image showing the L- and R-areas from both sides of the step.

More specifically, in the perpendicular direction the periodicity of the intensity distribution is depended on the change of the unit cell parameters along [0001]. So the fitting parameters for the two discrete parts of the micrograph from both sides (noted as L-area and R-area in Fig. 7-14) show small but detectable differences. Fig. 7-15 presents the deviation of the experimentally measured layers’ position, as compared to the “ideal” unshifted deduced from the periodicity obtained by the fitting function.
Fig. 7-15: The deviation of the actual-experimental position of the close packing layers from the calculated, using the fitting parameters as a function of the layers numbering.

The blue colored line shows the deviation referred to the parameters computed for the SiC substrate and the red colored one for the AlN epilayer. The shifting clearly increases sharply on the interface (noted with a perpendicular dashed line) indicating the changing of periodicity and the position of the interface. Moreover, the deviations do not suggest any systematical or significant strain along c-axis, with values of around 5%.

Fig. 7-16: Graph showing the layer’s numbering vs the shifting between the successive layers.

In Fig. 7-16, the plot shows the displacement of the right part layers along [0001] direction (R-area) relatively to those of the left part (L-area) (from both sides of the step). The continuous horizontal lines (noted as averAlN and averSiC) represent the average value of the AlN and SiC layers’ shifting respectively. It is easily detected that each layer keeps its
position along [0001] direction in both sides of step, without any significant strain or
displacement (the y- vertical axis varies from ~0.12 to 0.07 with an average value ~0.03).

In the following paragraphs, the atomic models of this stepped interface are suggested and
discussed and the simulations are performed.

### 7.2.4 Atomic models and computer simulations

As already mentioned, the energetically favourable bonding in the AlN/SiC (GaN/SiC)
interfaces is Al-C (Ga-C) and N-Si. Moreover, F. A. Ponce et al. [153] showed that for
atomically abrupt and planar interfaces, the N-C and Si-Al bonds can be excluded as
possibilities, due to the different bond length and Z number (atomic number), resulting to
difference in intensity in the TEM image. Table 7-1 presents Z number and bond length for all
possible bonding configurations in the SiC/AlN interface. More specifically, the Si-C and Al-
N exhibit bond lengths of 1.88 and 1.89 Å, respectively, with a sum of Z of 20 for both of
them. On the other hand, the N-C bond is shorter in comparison with the Si-C and Al-N, and
because of its Z number (13), a darker line of spots should be observed. Moreover, Si-N
bonding configuration has a much closer value of bond length and also a Z number of 21,
making it a dominant bonding configuration in the interface. In the same way, Al-C (and Ga-
C) bond length is near enough to the Si-C and Al-N bond length, with a similar Z number.
Furthermore, compounds containing Si-Al (Si-Ga) bonds are not commonly observed in
nature and have a much longer bond length. However, in the STEM images presented in the
previous chapter, a different contrast (Z number) monolayer of Ga was observed in the 6H-
SiC/AlN interface, so it also has to be taken into account.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Sum of Z</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-C</td>
<td>20</td>
<td>1.88</td>
</tr>
<tr>
<td>N-C</td>
<td>13</td>
<td>1.47</td>
</tr>
<tr>
<td>Al-C</td>
<td>19</td>
<td>2.06</td>
</tr>
<tr>
<td>Al-Si</td>
<td>27</td>
<td>2.43</td>
</tr>
<tr>
<td>N-Si</td>
<td>21</td>
<td>1.74</td>
</tr>
<tr>
<td>Al-N</td>
<td>20</td>
<td>1.89</td>
</tr>
<tr>
<td>Ga-N</td>
<td>38</td>
<td>1.95</td>
</tr>
<tr>
<td>Ga-Si</td>
<td>45</td>
<td>2.67</td>
</tr>
<tr>
<td>Ga-C</td>
<td>37</td>
<td>2.03</td>
</tr>
<tr>
<td>Si-C</td>
<td>20</td>
<td>1.88</td>
</tr>
</tbody>
</table>

**Table 7-1:** Z number and bond lengths for AlN and GaN/SiC bonding configurations [153], [154].

Finally, in our case, we consider the possible atomic bonding configurations for the
interface for the (0001) SiC lattice with Si at the top of the ⟨11̅20⟩ dumbbell, based on the
previous analysis. More specifically, we take into account only the Si-N bonding
configuration in the AlN/GaN/SiC interface that is in agreement with our observations. Thus,
the atomic model shown in Fig. 7-17 is proposed, illustrating a one-bilayer step structure in the 6H-SiC/GaN/AlN interface, with the characteristic alteration in stacking sequence around the step. The quantitative analysis results showed an insignificant strain existence in the area around the step, thus no such addition was essential for the building of the model.

Based on this model, the computer simulation images are presented in the following paragraphs. It is very important to denote the intensity variations observed in the HRTEM image. The intensity profile shown in Fig. 7-18, clearly illustrates these variations. In the SiC area (left area of graph), intensity variations are observed per three layers or per twin direction of 6H-SiC. More specifically, the twin direction pointing from left to right is brighter than the twin pointing in the opposite direction. In the AlN layer, the same situation is displayed, with the intensity difference existing in one by one layer. This fact must be taken into account when simulating this area, by choosing the appropriate parameters in order to illustrate this intensity profile in the computer-simulated images.
The intensity variations observed in the HRTEM image can be explained by a small beam tilt in relation to the perfect ideal beam orientation. However, in the STEM-HAADF imaging results presented in Chapter 6, the intensity variations were also present in the AlN layer, in one by one layers, attributed to the presence of a different atomic number (Z) element, Ga. Thus, both beam tilt and presence of Ga could explain this intensity profile obtained in the HRTEM images results.

Furthermore, in the AlN layer, difference in intensity is also observed in an area close to the step, between the left part (before the step) and right part (after the step) of the structure. This situation is illustrated in Fig. 7-19. If for example, in the area before the step, in the same layer, the spots are bright, depending on the Al-N dumbbell direction, in the area after it the spots intensity is weaker.
Fig. 7-19: Intensity profile of the AlN layer (a) before the step and (b) after the step.

For the simulation, the Pierre Stadelmann's JEMS electron microscopy simulation software was used. For imaging, the multislice iteration method was used. After setting up the basic microscopy, imaging and multislice parameters, the resulted HREM map is shown in Fig. 7-20 for a set of defocus and thickness values. The defocus values are from -40 to 30nm and the thickness values are 1.2-8.6nm. However, a better similarity was found in the area with the positive defocus values. Thus, Fig. 7-21 shows the JEMS run results with defocus values from +20 to +45. Moreover, the atoms positions correspond to the black regions and not the white spots (Fig. 7-22).
**Fig. 7-20:** JEMS simulation results for A (0,0,0), L(0,0,0) (A: optical axis, L: Center of Laue zone). Defocus values from -40nm to +30nm, Thickness values from 1.2nm to 8.6nm.
Fig. 7-21: JEMS simulation results for A (0,0,0), L (0,0,0) (A: optical axis, L: Center of Laue zone). Defocus values from +20nm to +45nm, Thickness values from 1.2nm to 8.6nm.
The optimal defocus-thickness set matching better our HRTEM image is (30nm-3.7nm), as presented in Fig. 7-23.

![Fig. 7-22: Simulation result proving that atoms correspond to the black regions of image](image1)

![Fig. 7-23: Best matching set of defocus-thickness values (30nm-3.7nm)](image2)

However, the intensity of the bright (spots) and dark regions (atoms) is the same all over the structure. By introducing a small beam-illumination tilt (change of optical axis centre from (0,0,0) to (+1.5,0,0)), and starting the calculations for the same set of defocus-thickness values, the resulting HREM mapping (Fig. 7-24) displays an intensity difference in the twin directions of the SiC as well as in the AlN layer, with the atoms positions corresponding to the black areas (for defocus 30nm), matching well to our TEM observation results.

Similarly, as observed in the experimental HRTEM image, in the 6H-SiC region, the twin direction pointing from the right to the left shows a weaker intensity of spots than the twin pointing in the opposite direction. Moreover, in the AlN layer, the intensity is stronger in one by one layers.
Fig. 7-24: JEMS simulation results for A (1.5,0,0), L (0,0,0) (A: optical axis, L: Center of Laue zone). Defocus values from +20nm to +45nm, Thickness values from 1.2nm to 8.6nm.
This difference in spots intensity in the computer simulation map is better presented in the graph below (Fig. 7-25):

**Fig. 7-25**: Intensity profile of the total structure, obtained from the computer-simulated image, showing the difference in intensity.

**Fig. 7-26**: Intensity profile of the (a) left and (b) right part of the AlN layer.
The tilting of the Al-N dumbbell, denoting either the AaCcAaCc… (left part of structure) or the BbCcBbCc… (right part of structure) layers sequence, is depicted as difference in the intensity profile between the right and left part of structure. The intensity profile taken from the computer simulated image along an area in the AlN layer, in both left and right region is presented in Fig. 7-26, reflecting the intensity difference situation in the area close to the step, as previously described.

By introducing not only a beam tilt but also a crystal tilt, the computer-simulated results are almost the same. The crystal tilt was performed by changing the center of Circle Laue (CLC), from (0,0,0) to (+11,0,0), equivalent to 0.59 deg. tilting. The change of CLC resulted in a small shifting of the crystal structure with no significant difference in the simulation results (Fig 7-27). Thus, the computer-simulated image introducing only the beam tilt is sufficient for the structure confirmation and the intensity variations explanation, coinciding well to the experimental HRTEM image.
Fig. 7-27: JEMS simulation results for A+5, L+11 (0.59 deg.)
Finally, for D (defocus) 30 nm and t (thickness) 3.7 nm, the computer simulated image fits well to the experimentally obtained HRTEM image. More specifically, the HRTEM image with the atomic model and the simulation results are presented in Fig. 7-28 (a) and (b).

**Fig. 7-28:** (a) HRTEM image with the model coinciding very well, (b) HRTEM image with the computer simulated image for D=30 and t=3.7, coinciding very well.
Chapter 7: Quantitative analysis

7.3 Results for 6H-SiC/AlN interface (#TG2134)-strained step

As already mentioned, the strain analysis (Fig. 6-19) showed the existence of several stressed areas on the SiC/AlN interface. These areas are connected with the presence of some steps on the SiC surface. However, there are also cases of steps not connected to stressed areas. In this paragraph, we present the study of a stressed area based on the previous analysis. We again considered four parts of the experimental micrograph around the step on the SiC substrate and measured the intensity distribution along to directions parallel and perpendicular to the SiC/film interface. Especially for the [0001] direction we estimated the intensity taking into account a relatively wide area in order to overcome the shifting of the closed-packed layers and perform fittings of the intensity along lines parallel and perpendicular to the SiC/film direction.

7.3.1 Horizontal analysis results

Based on previous analysis, in Fig. 7-29, the white colored areas numbered from 1 to 57, in the left part of the HRTEM image, indicate the area around the step where the intensity distribution along these lines is measured and then fitted using the sine function (7-1):

![HRTEM image with white colored areas noted](image.png)

**Fig. 7-29:** A HRTEM image with the white colored areas noted.

The same procedure was repeated for the right part of image, without including the center part, where a defected and strained area exists. In Fig. 7-30, a characteristic plot, resulting from the horizontal analysis, shows the phase shift of the fitting of the intensity’s distribution along a line that corresponds to the projection of a close-packing layer. Thus, this graph reveals the stacking sequence and therefore the starting position of the AlN epilayer.
Moreover, the comparison of the sequence clearly shows the height of the step and any alteration on the stacking sequence between the two parts of the image.

More specifically, in this graph, the left and right parts of the image are represented by the red and blue colored graph respectively. It is clearly observed that the lower part of the micrograph (left part on the plot) obviously follows the sequence \( + + + - - - \ldots \) that denotes the stacking for the 6H-SiC in Hägg notation, while the upper part follows the sequence for the hexagonal AlN \( + - + - \ldots \). On the other hand, a difference in the stacking sequence is obvious in the right part of the graph for both parts of the image. Indeed, after comparing the stacking sequence obtained from the left part of the image (red colored line on the plot) with the sequence from the right one (blue colored line on the plot) a characteristic alteration is clearly shown, denoting a stepped interface and confining the step height. More specifically, the 6H-SiC sequence is continued until the 77th layer on the left part of the image, whereas on the right part it is continued until the 75th layer.

In this case too, the exact starting position of the AlN is not clear; e.g., the AlN stacking sequence is indicated in the graph from the 76th layer (making it possible to have started growing either in the 76th or the 77th layer) and for the right part of image (76th or 75th layer). Moreover, the resulted sequence gives two possible options for the AlN epilayer starting position. More specifically, a one-bilayer step or a two-bilayers step could have been formed in the SiC surface.

A characteristic graph, shown in Fig. 7-31, presents the periodicity of the position of the close packing layers along \([1\bar{1}00]\), revealing any strain situation existing. More specifically, the red colored graph represents the periodicity (as calculated using the fitting parameters) for the left part of image and the blue colored graph for the right part of image. The graph is split into three parts: from the beginning until around the 75th layer (which is different for the left and right part of image), from around the 75th layer until 91st layer and finally from the

**Fig. 7-30**: Characteristic plot of the alteration of the phase shift across the stacking layers (d indicates the interatomic distance along the direction parallel to the interface that corresponds to the projection of a close-packing layer), revealing the position of the step. The layer’s numbering begins from the bottom of the image.
91st layer until the 100th layer. For every part of the graph, the average values for periodicity for the left and right part of image are denoted with a dashed and solid line respectively.

For both parts of the image (left and right), it is clearly observed that in the area around the 75th layer and before it, where the 6H-SiC substrate exists, the calculated periodicity is found in between 24.9 and 25.1. On the other hand, after the area 75th-77th layer, in the AlN epilayer area, in the first layers after SiC/AlN interface an increase of the periodicity (around 25.15-25.25) along [1100] is presented, indicating the starting position of the AlN epilayer. However, after around 91st layer, the periodicity shows an increase, indicating a very small local distortion (the periodicity values reach 25.4).

Thus, in the area around the step, the deviations do not suggest any systematical or significant strain along [1100], exhibiting a deviation of maximum 1% in the SiC area and AlN layer. Moreover, the left as compared to the right part calculated periodicity presents a small and thus negligible deviation.
Chapter 7: Quantitative analysis

7.3.2 Vertical analysis results

Based on previous analysis, in Fig. 7-32, the white colored areas (L and R-area), indicate the area around the step where the intensity distribution along these line is measured and then fitted using the sine function (7-1):

Fig. 7-32: HRTEM image showing the L- and R-areas from both sides of the step.

More specifically, in the perpendicular direction the periodicity of the intensity distribution depends on the change of the unit cell parameters along [0001]. So the fitting parameters for the two discrete parts of the micrograph from both sides (noted as L-area and R-area in Fig. 7-28) show small but detectable differences. Indeed, Fig. 7-33 presents the deviation of the experimentally measured layers’ position, as compared to the “ideal” unshifted ones, deduced from the periodicity obtained by the fitting function. The L- and R-area are splitted into L-SiC, L-AlN and R-SiC, R-AlN respectively and shown separately in this graph.
Fig. 7-33: Characteristic graph showing the deviation of the actual-experimental position of the close packing layers from the calculated, using the fitting parameters as a function of the layers numbering.

More specifically, the blue colored line shows the deviation referred to the parameters obtained for the R-area AlN epilayer and SiC substrate and the red colored one for the L-area AlN epilayer and SiC substrate. The shifting clearly increases sharply on the interface (noted with a perpendicular dashed line) in all cases, indicating the changing of periodicity and the position of the interface. Moreover the deviations do not suggest any systematical or significant strain along c-axis ([0001]). Only a small part of the L-AlN epilayer, near the interface area (layers around 73-80 in the graph), exhibits locally a greater but not significant value of deviation, as compared to the others.

In Fig. 7-34, the characteristic plot illustrates the displacement of the left part layers (L-area) along [0001] direction relatively to those of the right part (R-area), from both sides of the step, covering a wide area before and after the step. This graph reveals very small displacements in the SiC area far away from the SiC/AlN interface. However, as approaching the interface, in the area between layers 60-100 (as shown in graph), the situation changes and an abrupt increase of displacement is clearly observed, indicating a strained area around the interface. Finally, after the 100th layer, the displacement reaches its maximum position, presenting small deviations around it.
Fig. 7-34: A graph showing the displacement of the left part layers (L-area) along [0001] direction relatively to those of the right part (R-area), from both sides of the step versus the layer’s numbering (from bottom to top).

The continuous black line represents the non-linear curve fitting of the data using a step function according to the equation:

\[ y(x) = A_2 + \frac{(A_1 - A_2)}{1 + e^{\left(\frac{x-x_0}{\sigma}\right)}} \]  

(7-2)

These results clearly reveal a characteristic strain around the SiC step and allow us to include an accurate displacement in the structural model following in the next paragraphs. More specifically, in the steps area, for the computation of the precise position of the atoms, a relocation by one layer is essential in the right part of the structure.
7.3.3 Atomic models and computer simulations

In this case, we consider the possible atomic bonding configurations for the interface for the (0001) SiC lattice with Si at the top of the \(\langle 11\bar{2}0\rangle\) dumbbell, based on the previous analysis. More specifically, we take into account only the Si-N bonding configuration in the AlN/SiC interface that is in agreement with our observations. Moreover, we have to take into account that as moving from the left to the right part of the structure, a downward inclination was observed and computed in the previous paragraphs analysis. The most possible interpretation in this case is the presence of a two-bilayers step on the SiC surface. In all other examined cases, non-strained areas were found in the steps positions, which, based on the STEM-HAADF and STEM-EDX analysis results, were one-bilayer steps.

Thus, the atomic model shown in Fig. 7-35 is proposed, illustrating a two-bilayers step structure in the 6H-SiC/AlN interface, forcing the inclination of the overgrown AlN epilayer and resulting to a stressed SiC area, until stability of layers is again observed.

\[\text{Fig. 7-35: Atomic model describing the strained step in the AlN/GaN/6H-SiC interface.}\]
Fig. 7-36: JEMS simulation results for A (0,0,0), L (0,0,0) (A: optical axis, L: Center of Laue zone).
Defocus values from -40nm to +30nm, Thickness values from 1.2nm to 8.6nm.
For imaging, the multislice iteration method was used. After setting up the basic microscopy, imaging and multislice parameters, the HREM map shown in Fig. 7-36 includes the multislice iteration method run results for a set of defocus and thickness values. The defocus values are from -40 to 30nm and the thickness values are 1.2-8.6nm. Moreover, the atoms positions correspond to the black regions and not the white spots. A better similarity was found in the area with the negative defocus values.

It is very important to denote the intensity variations observed in the HRTEM image. The intensity profile shown in Fig. 7-37 (b), taken from the selected area of Fig. 7-37 (a), clearly illustrates these variations. More specifically, in the SiC area (left area of graph), intensity variations are observed per three layers or per twin direction of 6H-SiC. More specifically, the twin direction pointing from right to left is brighter than the twin pointing in the opposite direction. In the AlN layer, the same situation is displayed, with the intensity difference existing in one by one layer (depicting the tilting of the layers in the 2H structure e.g. from Aa to Bb). This fact must be taken into account when simulating this area, by choosing the appropriate parameters in order to illustrate this intensity profile in the computer-simulated images.

Fig. 7-37: (a) A HRTEM image with the area noted, (b) Intensity profile along this area.
The intensity variations observed in the HRTEM image can be explained by a small beam tilt in relation to the perfect ideal beam orientation. However, in the STEM-HAADF imaging results presented in Chapter 6, the intensity variations were also present in the AlN layer, in one by one layers, attributed to the presence of a different atomic number (Z) element, Ga. Thus, both beam tilt and presence of Ga could explain this intensity profile obtained in the HRTEM images results.

Thus, by repeating the JEMS run, after introducing a small beam-illumination tilt (change of optical axis centre from (0,0,0) to (-1.5,0,0) (Fig. 7-38), and starting the calculations for the same set of defocus-thickness values, the resulting HREM mapping displays an intensity difference in the twin directions of the SiC as well as in the AlN layer, with the atoms positions corresponding to the black areas (for defocus 30nm), matching well to our TEM observation results.
Chapter 7: Quantitative analysis

Fig. 7-38: JEMS simulation results for A (-1.5,0,0), L (0,0,0) (A: optical axis, L: Center of Laue zone).
Defocus values from -40nm to +30nm, Thickness values from 1.2nm to 8.6nm.
Finally, for D (defocus) -10nm and t (thickness) 3.7 nm, the computer simulated image fits well to the experimentally obtained HRTEM image. More specifically, the HRTEM image with the atomic model and the simulation results are presented in Fig. 7-39, on the right and left part of image respectively. The simulation resulted image does not present recognizable differentiations claiming for a stacking sequence change.

Fig. 7-39: A HRTEM image with the simulation results and model presented as insets (on the left and right part respectively).
Conclusions

In this thesis, the structural characterization of homoepitaxially and heteroepitaxially grown epilayers on “on axis” and off axis SiC and Si substrates is studied and discussed. Firstly, 4H-SiC epilayers were grown on 2 deg 4H-SiC substrates, using N2O post-deposition annealing or N2O post-deposition annealing, for MOS capacitors applications. The effect of chemical mechanical planarization process (CMP) on the structural and electrical characteristics of the structure is discussed. In both cases (after N2O/POCl3 post deposition annealing), before CMP treatment, the 4H-SiC surface presents a step-bunching situation (parallel to [11-20]), where the most dominant step height is four (4) bilayers of Si-C, which corresponds to the unit cell of 4H-SiC. In addition, no epitaxial-induced defects are observed, like pits and triangular defects, which could degrade devices’ performance. Moreover, the oxide layer treated in POCl3 exhibits in its surface fewer undulations (steps) along the [11-20] direction, exhibiting a high degree of planarization in respect to the N2O treatment situation. Thus, a different surface morphology of the oxide treated in POCl3 is observed, as a consequence of the strong incorporation of Phosphorus in the oxide layer during annealing procedure, passivating the interface states and so enhancing the channel mobility. Finally, the CMP process results in a good quality SiO2/SiC interface, where the 4H-SiC interface becomes smooth enough (presenting 1-2 atomic layers height), with only some few cases of greater steps height.

Concerning the electrical behavior before and after CMP process, the electrical characterization showed an increased value of the oxide electric breakdown field after using CMP process. Moreover, these results as well as the computed interface state density in the low $1 \times 10^{12}$ eV$^{-1}$cm$^{-2}$ range are comparable with the results that have been typically measured in the case of 4 deg off-axis 4H-SiC substrates, paving the way to the 2 deg off oriented SiC substrates device fabrication.

Furthermore, AlGaN/GaN buffer heterostructures were grown on “on axis” and 4 deg off Si (111) substrates by MOVPE method. The electron microscopy study reveals the very good epitaxial growth of the layers. Almost c-plane orientated nucleation grains are achieved after full AlN layer growth. During growth, the step graded AlGaN buffer inserted in between the GaN layers, behaves as a defect filter, preventing the threading dislocations existing in the first grown layers from propagating into the GaN layer (grown after the AlGaN layers), with the greater part of them not reaching the AlGaN/GaN heterostructure and thus enhancing the 2DEG channel electron density. Thus, a crack-free smooth surface of the final GaN epitaxial layer is achieved in both cases, making the buffer structure ideal for the forthcoming growth of the heterostructure (used for HEMT device applications). Finally, the growth of the AlGaN/GaN heterostructure on top presents characteristic and periodic undulations (V-pits) on the surface, due to strain relaxation reasons. The AlN interlayer grown in between the heterostructure demonstrates an almost homogeneous thickness, probably reinforcing the 2DEG electrical characteristics.

Additionally, AlGaN/GaN heterostructures were also grown on “on axis”, 1 deg and 2 deg off SiC (0001) substrates by MOVPE method. The very good epitaxial growth of the layers,
Conclusions

one on top of the other, was revealed by electron diffraction study. In all cases, the GaN epilayer is free of cracks but in the “on axis” substrate shows a higher density of TD as compared to the misoriented one. However, in every case dislocation density decreases sharply as moving towards the structure surface. V-shaped structures are formed into the AlN nucleation layer (with [101\text{-}10] sidewalls), completely overgrown by GaN in all samples, but are smaller and better defined in the on axis case. Moreover, the V-pit density is larger in the off axis case, probably due to the higher step density.

A vertical defect formation is observed in the steps positions (mostly one-bilayers) of SiC/AlN interface in the case of 1 and 2 deg cut off substrates, which is caused by the stacking mismatch between the different AlN domains. This defect, called stacking mismatch boundary (SMB), practically denoting a perfect twin, mostly results in the V-shaped defect formation. In all HRTEM and STEM images results, we deduced the presence of SMBs at the apex of the V-shaped defects. Thus, these defects, in fact, represent V-trenches. However, we cannot exclude the possibility of V-pits presence in other regions. In some cases the SMBs are terminated by stacking faults, without forming any V-defects. However, in some steps positions, no SMBs are formed. In the on-axis substrates case this phenomenon is not so common, due to the almost zero steps density. Furthermore, by using advanced microscopy techniques, a monolayer of GaN is revealed in the SiC/AlN nucleation layer interface, which follows the stacking sequence of the substrate grown on, probably because it is energetically more favourable than start using the new layers sequence.

The AlGaN layer of the AlGaN/GaN heterojunction in the on axis sample, exceeding the critical thickness, presents a characteristic undulation in forms of V-pits creation, formed due to strain relaxation reasons. The off-cut of 2 deg gives the best morphology (atomically flat) of the AlGaN barrier and GaN cap layers, despite the steps in the SiC/AlN interface, exhibiting the best electron mobility values. It is important to mention that no step-bunching is observed in the AlN/SiC interface. Thus, the use of 2 deg off SiC substrates for GaN based-devices epitaxy is feasible.

Moreover, quantitative results are obtained by applying a simple sinusoidal fitting in any direction in a HRTEM micrograph, important for the building of models. More specifically, the periodicity (w) extracted from the sine fitting results, denotes the spots periodicity in the HRTEM image in the specific direction, and thus the lattice constants of the elements and any strain existing along [1\text{1\text{-}00}] as well as along [0001] c-axis. Furthermore, the phase ($\chi_c$) of the sine function represents the wave propagation characteristics. Thus, by comparing the phase ($\chi_c$) for successive rows of dots, the shifting between them can easily reveal the sequence of the stacking and also any disturbance existing. Thus, in this way, it is possible to perform the fitting over the whole intensity distribution or over discrete parts of it, in order to highlight better the differences that exist among the several parts of the image.

More specifically, after examining two cases: (a) a one-bilayer step with no significant strain existing, (b) a two-bilayers step with significant strain existing around it, the quantitative results in combination with the TEM/STEM-EDX results, were used in order to build the appropriate models for the SiC/AlN interface. Indeed, the resulted simulated images
are found to coincide well to the experimental TEM micrographs, confirming the accuracy of the models and thus the quantitative analysis method proposed.

Finally, the results of this thesis showed that GaN heteroepitaxy and SiC homoepitaxy can be successfully introduced onto 2-deg-off SiC substrates, paving the way to monolithic integration of both kinds of devices on a common platform of SiC.
Future work

The 2D-GaN formation in the SiC/AlN interface, which was observed in both on axis and off axis samples, constitutes a very important fact, obtained from STEM-HAADF/EDX analysis results. Concerning this thesis purpose, its presence could affect the electrical properties of the heterostructure and thus affect the HEMT structure quality. So far, its presence has not yet been scientifically reported in this exact form. In this thesis, its formation is attributed to a sort of memory effect, or to a Ga interdiffusion during GaN growth via the AlN layer.

As very recently reported, 2D nitrides are key to advancing novel devices: they present excellent electronic and magnetic properties, as well as ideal structure, indicating great potential application in future spintronics and tunable optoelectronics [144], [155]. Thus, a detailed theoretical and experimental analysis could easily indicate the origin of this monolayer, and the role that it plays in the 2DEGs channel characteristics and quality. Moreover, this analysis could also indicate other possible applications that it can be used and be advantageous at.

Moreover, the two-dimensional threading SMB defects forming at the SiC/AlN interface could be detrimental for the overall HEMT device quality. It is thus obvious that ways of defects elimination must be found, as for example having ideal steps heights on the SiC substrate, so that SMBs do not form.

Concerning the AlN/SiC substrate interface analysis described, using quantitative and STEM-EDX results, it is important to perform theoretical ab initio calculations, in order to obtain the relaxed configuration of atoms in the step and SMB areas.

Finally, the quantitative method described in this thesis, can be easily used for the analysis of other areas of this structure, as the V-shaped defects or the AlGaN/GaN heterostructure area, in order to reveal the stacking sequence existing and any disturbance of it. A user-friendly application for the automatic analysis of the fitted curves of the HRTEM image could be developed, for the facilitation of the procedure.
Conferences and Publications

Publications


International Conferences


2. The 16th European Microscopy Congress (EMC2016), 28/08-02/09/2016, Lyon-France, Poster presentation with title: Quantitative analysis of AlN/SiC interfaces in AlGaN/GaN heterostructures grown on SiC, A. Gkanatsiou, Ch. B. Lioutas, N. Frangis

3. 16th International Conference on Silicon Carbide and Related Materials (ICSCRM2015), 04-09/10/16, Giardini Naxos-Italy, Poster presentation with title: (a) Quantitative analysis of interfaces in multilayer structures grown on SiC, A. Gkanatsiou, Ch. B. Lioutas, N. Frangis and Poster presentation with title: (b) Processing and Characterization of MOS Capacitors Fabricated on 2°-Off Axis 4H-SiC Epilayers, M. Vivona, P. Fiorenza, T. Sledziewski, A. Gkanatsiou, M. Krieger, T. Chassagne, M. Zielinski, F. Roccaforte

4. 12th International Conference on Nanosciences and Nanotechnologies (NN15), 07-10/07/2015, Thessaloniki-Greece, Oral presentation with title: Quantitative analysis of interfaces in multilayer structures grown on SiC, A. Gkanatsiou, Ch. B. Lioutas

5. The Microscience Microscopy Congress (MMC2015), 29/06-02/07/2015, Manchester-UK, Poster presentation with title: Atomic models for 6H-SiC/AlN
interfaces in multilayer structures grown on SiC, A. Gkanatsiou, Ch. B. Lioutas, N. Frangis

6. 18th International Microscopy Congress (IMC2014), 7-12/09/2014, Prague-Czech, Poster presentation with title: Microstructural characterization of AlGaN/GaN heterostructures grown on low angle-off 4H-SiC substrates, Gkanatsiou, Ch.B. Lioutas, N. Frangis, P. Prystawko, M. Leszczynski

7. 11th International Conference on Nanosciences & Nanotechnologies (NN14), 8-11/07/2014, Thessaloniki-Greece, Poster presentation with title: Atomic models for interfaces in multilayer structures grown on SiC, A. Gkanatsiou, Ch. B. Lioutas, N. Frangis


9. 10th International Conference on Nanosciences & Nanotechnologies (NN13), 09-12/07/2013, Thessaloniki-Greece, Poster presentation with title: TEM study of thick GaN buffers on Si(111) substrates, A. Gkanatsiou, Ch. B. Lioutas, N. Frangis, E.K. Polychroniadis, P. Prystawko, M.Leszczynski

**National Conferences**


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**Scholarships**
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Fig. 6-53: Properties of 2D nitrides from ab initio hybrid density functional theory. (a) binding energy calculations of freestanding planar and buckled 2D nitrides (M: group-III metal element, N: nitrogen and H: hydrogen atoms), as a function of layer number (L), showing increased stability of the buckled structure resulting from their decreasing binding energies relative to planar 2D nitrides. (b) Band-structure calculations via DFT meta-GGA of freestanding planar and buckled 2D monolayer GaN, illustrating buckled 2D GaN with a direct bandgap (E_g) of 5.28 eV and planar 2D GaN with indirect E_g of 4.12 eV, both larger than the direct E_g of wurtzite bulk GaN (3.42 eV) due to quantum confinement. (c) Diagram of bandgap energy versus in-plane lattice parameter for bulk and buckled 2D nitrides, establishing the possibility of probing deep into the ultraviolet with monolayers of group-III nitrides. The E_g as a function of number of atomic buckled layers is included as an inset in (c) [144].

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